

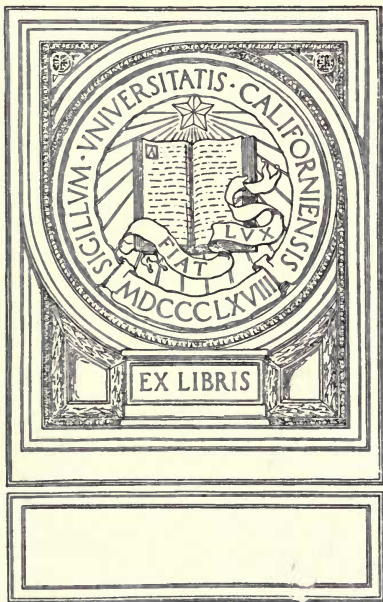
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LABORATORY MANUAL

CONTAINING

DIRECTIONS FOR A COURSE OF EXPERIMENTS
IN ORGANIC CHEMISTRY

SYSTEMATICALLY ARRANGED TO ACCOMPANY
REMSEN'S ORGANIC CHEMISTRY

REVISION OF 1922

BY

W. R. ORNDORFF, A.B., PH.D.

PROFESSOR OF ORGANIC CHEMISTRY IN CORNELL UNIVERSITY

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INTRODUCTION

The student is expected to be familiar with the General Part of Gatterman's *Practical Methods of Organic Chemistry*, translated by Schober and Babasinian, 3d American Edition, pages 1 to 77. Descriptions of the methods used in the Laboratory of Organic Chemistry will be found in this part of the book.

Before beginning any experiment the student is expected to read carefully the directions given in the Laboratory Manual for that experiment and to be sure that he understands them. If in doubt about any point he should consult the instructor or the assistant before beginning the experiment. He is urged to read ahead of the experiment he is doing, when opportunity presents itself, and he will find that it is frequently possible to be carrying on two or more experiments at the same time. It is necessary to use every minute in the laboratory to advantage in order to finish the required work in the allotted time.

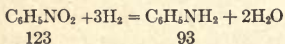
When the apparatus required for the experiment has been set up according to the directions given in the manual the student requests the assistant in charge of his section in the laboratory to inspect it. If the apparatus is satisfactory the student may begin the work. If it is not satisfactory the assistant will indicate what changes are necessary. The experiment is then performed by the student and the results are inspected by the assistant. Thus each experiment is checked at the beginning and at the end by the assistant, who also watches the student while the experiment is in progress. If the method of procedure is not correct or could be bettered, the student is at once informed of it. The directions given in the laboratory manual must be fol-

lowed very carefully or the experiment will fail and will have to be repeated. It is never necessary to repeat an experiment if the directions in the manual and the advice of the assistant are followed carefully.

Blank pages are provided in the manual so that any observations or data may be recorded immediately. The experiments should be written up as soon as possible after the experimental work is finished and in accordance with the following outline:

1. All the reactions involved in the preparation of the compounds, including all intermediate steps.
2. Observations and answers to questions. Sometimes questions are indicated by putting an interrogation mark in parentheses after a statement.
3. The percentage yield. The percentage yield of each compound prepared is determined by comparing the weight of the compound found with the theoretical amount calculated from the equation.

For example, in Experiment 49, suppose that 20 grams of aniline were obtained from the 40 grams of nitrobenzene used. The theoretical amount according to the equation:



is calculated from the proportion:

$$\begin{array}{l} 123 : 93 :: 40 : x \\ x = 30.24 \text{ grams of aniline.} \end{array}$$

As 20 grams of aniline were obtained the percentage yield would be:

$$\frac{20}{30.24} \times 100 = 66.1\%$$

From time to time the student will be called into the office of the instructor for an informal oral quiz covering the work finished. Questions will be asked on the laboratory procedure and on the theoretical part of the work. An attempt is made in these quizzes to make clear parts of the theoretical work that the student has confused or misunderstood and to find out if he knows what he has been doing.

Samples of the compounds made are saved and are shown to the instructor at the quizzes. These should be put in small homeopathic vials, labeled with the name of the substance, boiling point or melting point, date of preparation and name of the student.

In working in the laboratory the student must keep the glass ware and apparatus clean. *No dirty apparatus should be put away in the desk.* Neatness and order are essential for good work in the laboratory and will be insisted upon. Great care should be exercised in working in the Laboratory of Organic Chemistry. The student should remember that many of the organic compounds with which he works take fire readily and some of them are poisonous. There is no danger provided that ordinary care is taken and the directions are followed closely. In any work where especial precautions are necessary the attention of the student is called to it in the directions for the experiment.

Gas-tight goggles are provided for every student and they must be worn whenever there is any danger of injury to the eyes.

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LABORATORY MANUAL OF ORGANIC CHEMISTRY

EXPERIMENT 1 FRACTIONAL DISTILLATION

Arrange the apparatus as shown in Fig. I, using a 500 cc. distilling flask, a thermometer, a condenser and an adapter. The distilling flask is securely, but not too

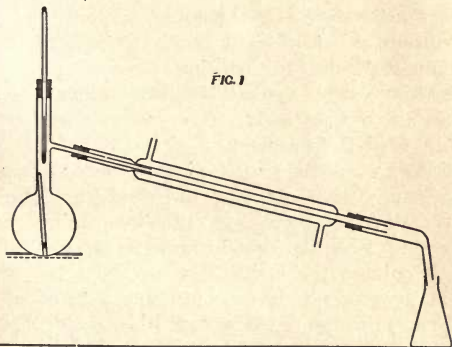


FIG. I

tightly clamped above the side tube. The side tube should extend into the inner tube of the condenser below the level of the water in the surrounding water jacket. The corks should be well bored and fit tightly and the apparatus arranged so that the liquid never comes into contact with the cork. The distilling flask should rest in a circular opening (diam. 2 in.) in a 6 in. square of asbestos board,¹ which should extend beyond the sides

¹ See *Identification of Pure Organic Compounds*, by Mulliken, vol. I, pp. 221, 223.

of the distilling flask. It should be made to fit tightly in the opening by moistening the edge of the opening and rotating the flask on the moistened edge. The ebullator tube¹ should be at the center of this circular opening. A 6 in. square of wire gauze, which is to be heated by means of a Bunsen burner, is placed under the asbestos board on an iron ring. The gauze should be bent down so that there is about a quarter of an inch air space between it and the flask. Have six clean, dry 250 cc. Erlenmeyer flasks, labeled to receive the fractions outlined in Table I (page 4).

Put 200 cc. of distilled water and 200 cc. of alcohol (95% ethyl alcohol) in the distilling flask and thoroughly mix them.

First Fractionation.—Heat the mixture slowly and note the temperature at which it begins to boil (when the first drop of the distillate falls into the receiver). Distil the mixture slowly, so that the drops falling into the receiver are distinct and can be counted (90–100 per minute), until the temperature of the vapor begins to exceed 83°, when the first receiver is replaced by the second one without stopping the distillation. Collect the distillate in this receiver until the temperature begins to exceed 88° when the second receiver is replaced by the third. Continue the distillation, collecting the distillates in the proper receivers, until only 5–10 cc. of the liquid remain in the distilling flask when the distillation is stopped.

Measure and record the volumes of each fraction and of the residue in Column 1, Table I.

Second Fractionation.—Put the first fraction in a clean, dry 250 cc. distilling flask. Distil this until the temperature begins to exceed 83°, collecting the distillate in the receiver just emptied. Note that all of the fraction does not distil over at this temperature. Stop the distillation and add to the residue in the distilling flask the

¹ See *Identification of Pure Organic Compounds*, by Mulliken, vol. I, pp. 221, 223.

second fraction, 83–88°. Fractionally distil this mixture, collecting the distillate in receivers 1 and 2, until the temperature begins to exceed 88°, when the distillation is again stopped and fraction 3, 88–93°, is added. Continue this procedure with each of the remaining fractions obtained in the first fractionation. Stop the distillation when about 5 cc. remain in the distilling flask.

Measure and record the volumes of the new fractions and of the residue in Column 2, Table I (page 4).

TABLE I

FRACTIONS	DISTILLATIONS				
	1	2	3	4	5
—83°					
83–88					
88–93					
93–98					
98—					
Residues					
Totals					

Compare the volumes of the same fractions in the two columns and draw your own conclusions regarding the results. What would happen if this procedure was repeated a third and fourth time?

Define the boiling point of a liquid and explain how the boiling point of a pure liquid could be determined by using the above apparatus.

For further information regarding all kinds of distillation and for methods of determining boiling points the student is referred to *Distillation; Principles and Processes*, by S. Young.

EXPERIMENT 2

FRACTIONAL DISTILLATION WITH A HEMPEL DISTILLING TUBE

Use a 500 cc. round bottom (R.B.) flask and a Hempel distilling tube (Fig. II) which is nearly filled with small, hollow, thin walled glass balls or small glass beads and connected with a thermometer tube, thermometer and a condenser. The R.B. flask should rest in the circular opening in the square of asbestos board and the wire gauze is placed about a quarter of an inch below the flask. The condenser is fitted with an adapter as in the first experiment. Clean and dry the Erlenmeyer flasks used as receivers in the first experiment to receive the distillates of this experiment.



Put 200 cc. of distilled water and 200 cc. of alcohol in the R.B. flask and mix thoroughly. Use an ebullator tube and heat slowly and note the temperature at which the mixture begins to boil. Distil *slowly* and *regularly*, collecting the fractions at the same temperature intervals as in Experiment 1, in the proper receivers. Stop the distillation when only 5-10 cc.

remain in the R.B. flask.

Measure the volumes of the fractions thus obtained and record them in a table.

Compare the results of Experiments 1 and 2 and draw your own conclusions regarding the two methods.

EXPERIMENT 3

DETERMINATION OF THE MELTING POINT

Use the Thiele apparatus, Dennis modification.¹

The pure substance, the melting point of which is to be determined, is finely ground and a portion of it put in a thin walled glass tube about 1 mm. in diameter and 6 cm. long which is sealed at one end. These *melting point tubes* can be obtained from the stock room or can be made by drawing out a piece of soft glass tubing in the flame of a Bunsen burner. A small amount of the substance is placed in the open end of the tube and is forced to the bottom by lightly



A

FIG. III

rubbing a file across the side of the tube. The upper end of the tube is fastened to the thermometer by means of a small rubber band (a thin section of rubber tubing will do) or a platinum wire, so that the substance is opposite the mercury bulb. The thermometer bulb is then immersed in the conc. sulphuric acid which should fill the Thiele tube so as to just close the opening of the side tube. The thermometer is supported in the apparatus by means of a cork, part of which is cut away so that the graduations of the thermometer may be seen. Heat slowly with a small flame of a Bunsen burner at the point A. Note the temperature at which the substance melts. The first determination only gives an approximate idea of the melting point and must be repeated to obtain the true melting point.

The heating may be fairly rapid until within about 15–20° of the melting point and then *it must be slow*, 3° a minute, *timed*, until the substance melts.

The sulphuric acid bath can be used up to 230°. For substances with higher melting points a mixture of 70

¹ *Jour. Ind. and Eng. Chem.*, 12, 366 (1920).

parts conc. sulphuric acid and 30 parts potassium sulphate is used.

Determine the melting points of naphthalene, urea and benzoic acid and of three unknown substances, all to be obtained from the instructor. *Wear goggles.*

Record the observed melting points in the following table and compare them with the correct melting points given in the text book.

TABLE II

SUBSTANCES	MELTING POINTS	
	Observed	Correct
Naphthalene		
Urea		
Benzoic acid		
Unknown 1		
Unknown 2		
Unknown 3		

Define the melting point of a substance. How can it be shown whether a compound is pure by determining its melting point?

Can the melting point be used to identify a compound?¹

EXPERIMENT 4

DETERMINATION OF THE BOILING POINT OF A SMALL AMOUNT OF LIQUID

Use the Thiele apparatus, Dennis modification, placing a few drops of the liquid in a small boiling point tube (a thin walled glass tube, sealed at one end, 5 mm. in diameter and 6 cm. long). A melting point tube should be used as an ebullator tube.

Determine the boiling point of chloroform and of an unknown substance, both to be obtained from the instructor. *Wear goggles.*

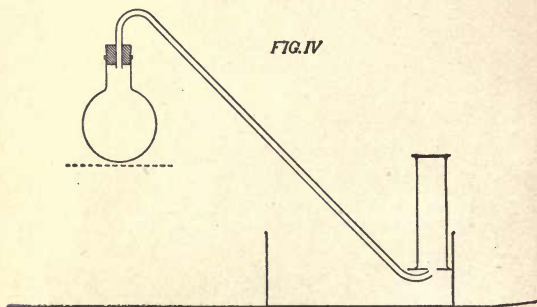
¹ See *Identification of Pure Organic Compounds*, by Mulliken, vol. I, pp. 3-4.

EXPERIMENT 5

METHANE

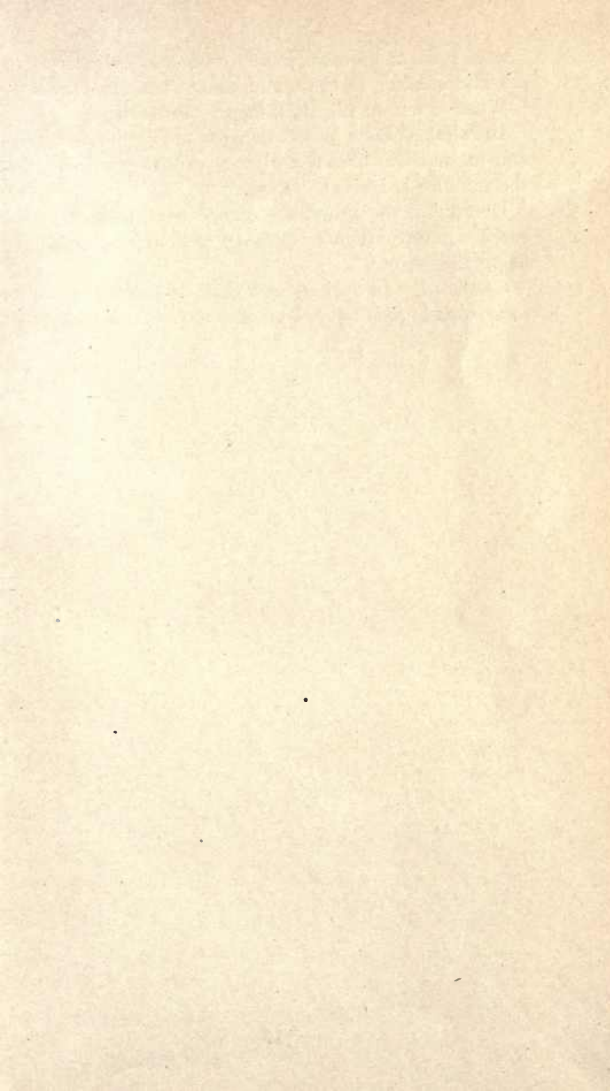
(Marsh Gas)

Grind together intimately 20 grams of *fused* sodium acetate and 40 grams of soda-lime. Put the mixture in a clean, dry 500 cc. R.B. flask. The flask is connected with a delivery tube as shown in Fig. IV. A square of



wire gauze is placed about one quarter of an inch below the bottom of the flask, but the asbestos board is not used. Heat the mixture with a triple burner collecting the first portions of the gas evolved over water in test tubes, discarding the first few until the air in the flask has been displaced. When the gas in the test tube *burns quietly* when ignited, collect the methane in small glass cylinders over water.

Ignite the gas in one of the cylinders and immediately after the gas is burned add 2 cc. of lime water and shake. Is a precipitate formed? Explain.



Add 1 cc. of bromide water to another cylinder of the gas and shake. Is there any color change? Explain.

What is left in the R.B. flask? Prove it.

In what volume proportions would you mix oxygen and methane to obtain the most violent explosion when the mixture is ignited? Explain.

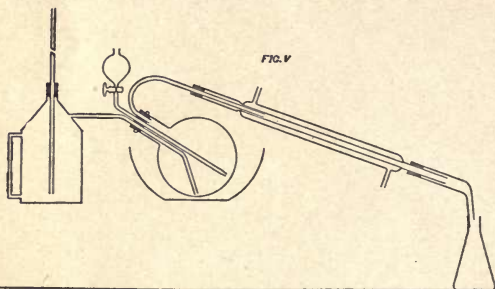
Determine the properties of the gas, including color, specific gravity (lighter or heavier than air), solubility, flammability, etc.

CAUTION. — *In working with gases all joints of the apparatus must be tight before beginning the experiment.*

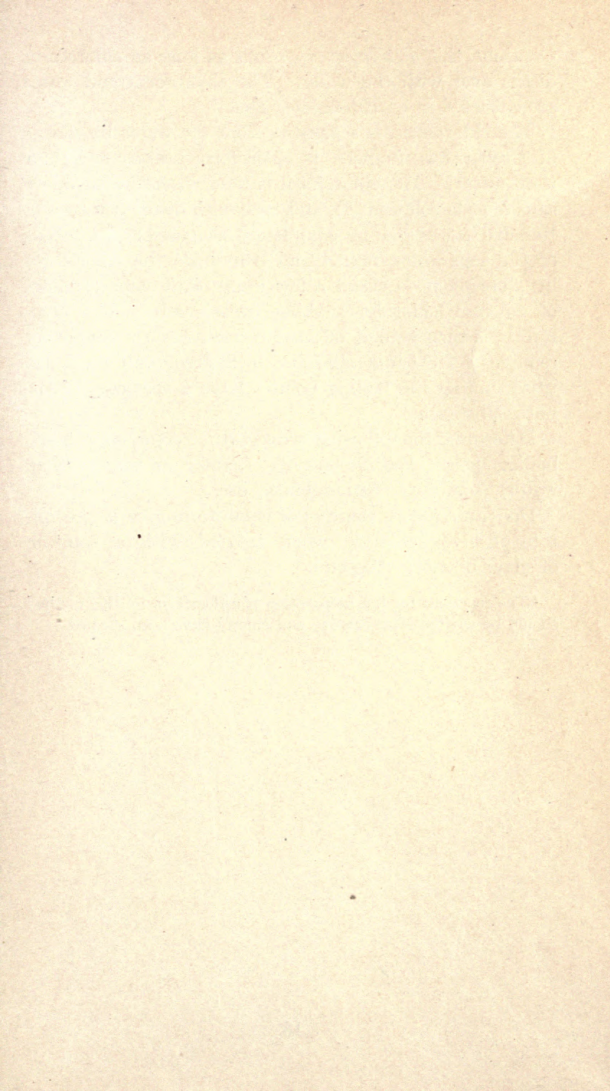
EXPERIMENT 6

CHLOROFORM

275 grams of bleaching powder and 800 cc. of water are put into a 3 liter balloon flask and thoroughly mixed. The flask is fitted with a cork having three holes.



Through one hole passes a separatory funnel, reaching to the bottom of the flask; through the second, a tube bent in two places and also reaching to the bottom of the flask; and through the third, the exit tube. The exit tube is connected to a condenser, which is attached to an adapter and the other tube is connected to a source of steam (if the laboratory desks are not equipped with steam, a small copper vessel may be used as shown in Fig. V or a R.B. flask may be used). Add very *gradually and carefully*, through the separatory funnel, a mixture of 22 grams of acetone and 70 cc. of water, shaking the flask during the addition. Chloroform will distil. Continue the shaking until chloroform ceases to come over. Then heat the flask and its contents in a water bath, at the same time passing steam into the flask.



Continue this *distillation in steam* as long as chloroform distils over with the water. The chloroform and water are collected in an Erlenmeyer flask.¹

The chloroform is separated from the water by means of a separatory funnel. Is chloroform heavier or lighter than water? The chloroform is then washed with dilute caustic soda solution (?), and then with distilled water(?). Remove the water as completely as possible by means of the separatory funnel and dehydrate the chloroform by allowing it to stand a few hours with some granules of calcium chloride, shaking occasionally. The chloroform is then poured off, and if necessary to completely remove the calcium chloride, is filtered, and then distilled, noting the boiling point. Save a specimen of the pure substance.

Determine the following properties:— color, odor, taste, boiling point, specific gravity (lighter or heavier than water), solubility, flammability, etc.

Does an aqueous solution of chloroform give a precipitate of silver chloride when treated with a solution of silver nitrate? Explain.

¹ The reactions for the preparation of chloroform by this method should be written after acetone and chloral have been studied.

EXPERIMENT 7

IODOFORM

Dissolve 10 grams of potassium iodide in 500 cc. of water and add 2 grams of acetone. To this mixture add through a separatory funnel slowly and with constant shaking, a dilute solution of sodium hypochlorite¹ as long as a precipitate is formed. Does any *iodide* remain in solution? Allow the precipitate to settle, decant off the supernatant liquid, wash by decantation with water two or three times, filter, dry on drying paper and crystallize from alcohol. To crystallize an organic solid prepare a saturated solution of the substance in the boiling solvent, using a reflux condenser if necessary. If the solution is not clear, filter while hot. Allow the solution to cool slowly in a R.B. flask or an Erlenmeyer flask. When cold filter off the crystals and dry them in the air on drying paper. Then distil off some of the solvent from the filtrate, allow the solution to cool and filter off the crystals formed. Continue this procedure until all of the iodoform has been crystallized. Which of the fractions thus obtained will be the purest and why? Save a sample of the pure iodoform. The reactions should be written after acetone and chloral have been studied.

Determine the following properties of the pure iodoform:—melting point, solubility in water and alcohol; crystal form, odor and color.

¹ The solution of sodium hypochlorite may be readily made by precipitating all the calcium in a saturated solution of bleaching powder with a solution of sodium carbonate. A slight excess of sodium carbonate will not interfere.

EXPERIMENT 8

ETHYL BROMIDE

(Hood)

100 grams of powdered potassium bromide are placed in a 500 cc. distilling flask, and a *cooled mixture* of 45 grams of 90% alcohol and 100 grams of conc. sulphuric acid is slowly added, keeping the flask and its contents cold by holding it in crushed ice and shaking. The flask is then connected with a condenser, using a similar apparatus to that shown in Fig. I, except that a 500 cc. suction flask, one quarter filled with ice water, is fitted to the adapter by means of a cork and used as a receiver. The side tube of the suction flask is connected with rubber tubing which leads to the hood exhaust (?). Surround the receiver with a freezing mixture (ice and salt). Heat the distilling flask until all the ethyl bromide has distilled. The ethyl bromide is then separated from the upper layer of water, washed in the separatory funnel, first with dilute caustic soda solution (?) and then with water (?). It is dried by allowing it to stand in a glass stoppered bottle with a few granules of calcium chloride for several hours with occasional shaking. The ethyl bromide is then poured into a small distilling flask and distilled, using a water bath and an ebullator tube. The entire apparatus must be clean and dry. Note the boiling point and save a sample of the pure product.

Determine its color, taste, odor, specific gravity (lighter or heavier than water) and flammability.

Add a little silver nitrate solution to some of the ethyl bromide. What happens? Boil the mixture and note what happens. Explain. What is formed when ethyl bromide is boiled with water?

What remains in the flask in which the ethyl bromide was made?

EXPERIMENT 9

FERMENTATION OF GLUCOSE

Dissolve 75 grams of glucose in 1 liter of water and add 30 cc. of a solution of Pasteur salts¹(?). Put the mixture into a 2 liter flat bottom flask and connect the flask by means of bent glass tubing with a cylinder containing lime water. The tubing extends to the bottom of the cylinder and the lime water is protected from the air by a layer of kerosene (?). Add to the mixture $\frac{1}{2}$ cake of yeast which has been mixed with a little water, forming a thick paste. Allow the mixture to stand for one week or until fermentation ceases. Filter off the supernatant liquid. Distil 500 cc. of this slowly through a Hempel tube, testing the *first* 5 cc. of the distillate for flammability. The rest of the distillate (about 20 cc.) is tested for alcohol as follows:—For each cc. of the cold aqueous solution of alcohol used add 2 drops of sodium hydroxide solution (1:10), then, drop by drop, add a concentrated solution of iodine in a solution of potassium iodide, until a barely perceptible tint of yellow, that persists after standing for several seconds, remains. If too much iodine should be used, cautiously add just enough of the sodium hydroxide solution to destroy the excess color. Let the mixture stand at the temperature of the laboratory for two minutes and then shake. Notice whether any iodoform separates. If no

¹The solution of Pasteur salts (based on an analysis of the inorganic constituents of the yeast plant) is made as follows:

Potassium phosphate.....	2.00 parts
Calcium phosphate.....	0.20 parts
Magnesium sulphate.....	0.20 parts
Ammonium tartrate.....	10.00 parts
Water.....	857.60 parts

iodoform separates in the cold, heat the solution to 60° and maintain this temperature for one minute. If the solution becomes entirely colorless during the heating, add just enough more iodine to restore the trace of yellow that was previously present. If no precipitate appears at once, set the tube aside for two minutes before making the final observation.

What is formed during the fermentation? What gas comes off?

See the article on "Fermentation" in Thorpe's *Dictionary of Applied Chemistry*.

EXPERIMENT 10

ABSOLUTE ALCOHOL

Break 500 grams of *good quick lime* into small lumps (not powder) and put it in a 3 liter balloon flask. Add 1 liter of 95% alcohol and exclude the moisture of the air by means of a cork carrying a tube filled with calcium chloride. Allow the alcohol to stand over the quick lime for at least two or three days. Connect the flask with a *reflux* (upright) condenser and heat the alcohol to boiling in a water bath for three hours. The upper end of the condenser should be closed by a cork carrying a tube filled with calcium chloride. Then fit the flask with a cork carrying a thermometer tube, and a thermometer and connect with a condenser. Heat the water bath and distil off the alcohol, noting the temperature at which it boils and using a suction flask as a receiver. Attach a tube filled with calcium chloride to the side tube of the suction flask. Care must be taken to prevent the alcohol from coming into contact with the moisture of the air. The distillate is to be tested with an *alcoholmeter* (by the assistant) to determine the percentage of alcohol. If it is not *absolute*, repeat the process with the distillate.

Add some white, anhydrous copper sulphate to some 95% alcohol and a little to some absolute alcohol. Note any change and explain.

Determine the properties of the absolute alcohol, including odor, color, taste, flammability. Does its vapor mixed with air explode? Does it solidify when cooled? What use is made of this fact? Is alcohol a good solvent?

Put the absolute alcohol in a glass stoppered bottle and save for future use.

Do not empty the waste lime into the sink; a suitable container will be found in the court.

EXPERIMENT 11

CALCIUM ETHYL SULPHATE

Add 90 grams of conc. sulphuric acid to 50 grams of alcohol in a small flask and heat the mixture on a boiling water bath for 30 minutes. What is formed? *Cool* the mixture and then pour it *slowly* and with constant stirring into a large porcelain dish containing crushed ice (?). Dilute with ice water to about a liter and a half. *Nearly* neutralize the acid by means of *slaked lime*, adding ice from time to time to prevent any rise of temperature (?). The solution is then filtered by the method of *reverse filtration*. The apparatus for this process consists of a small funnel which is covered with muslin. The stem of the funnel is attached by rubber tubing to a 500 cc. suction flask which is connected with the suction pump. The funnel is placed in the liquid to be filtered and the suction started. The filtered liquid is quickly drawn into the suction flask. The residue is now treated with 500 cc. of ice water, the mixture thoroughly stirred and the liquid filtered off. Clear limewater is now added to the combined filtrates to alkaline reaction (?), and this solution is evaporated to crystallization on a water bath. Calcium sulphate will separate as the solution is concentrated and this should be filtered off. Explain. After all the calcium sulphate has been removed the solution is allowed to crystallize and the crystals formed are filtered off, using a Buchner funnel. The process is repeated with the mother liquor. The crystals are drained thoroughly on the Buchner funnel and dried on drying paper.

Determine the color, taste, crystal form, and solubility of the crystals. Save a sample of the substance.

Does the salt contain water of crystallization? Does it contain carbon? Prove both statements.

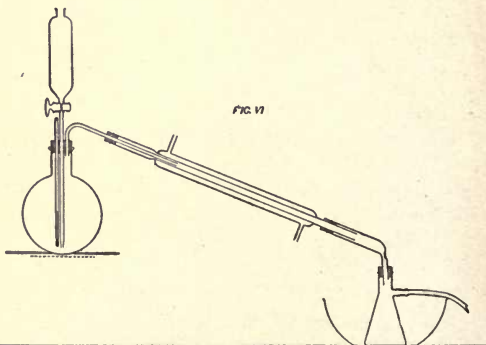
Dissolve some of the calcium ethyl sulphate in water and add a solution of sodium carbonate. Explain what takes place. Acidify some of the solution of calcium ethyl sulphate with hydrochloric acid and boil the solution. Add a few drops of barium chloride and note what takes place. Explain.

What is formed when ethyl sulphuric acid is heated with alcohol? When it is heated with water?

EXPERIMENT 12

ETHER

Arrange an apparatus as shown in Fig. VI, using a 2 liter balloon flask. The receiver, a suction flask, is surrounded by a freezing mixture (ice and salt) and rubber

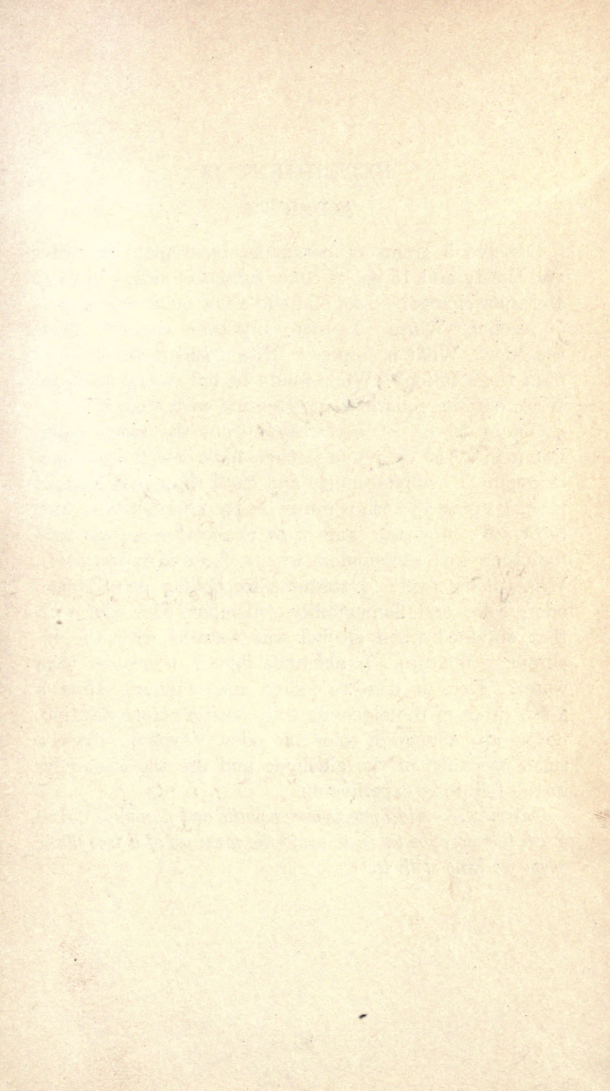


tubing which extends to the floor is attached to the side tube (?). Put in the flask 170 grams of alcohol, cool the flask and add slowly 306 grams of concentrated sulphuric acid. *Wear goggles*

Heat the mixture until the temperature reaches 127° to 128° . Then *cautiously* and *slowly* add through the separatory funnel a slow stream of alcohol in the form of *vapor bubbles*, regulating the flow of alcohol so that the temperature is kept between 127° and 128° and the volume of liquid in the flask is kept constant. When 200 cc. of ether have been obtained the operation is stopped. The distillate may consist of two layers, and contains, besides ether, water, alcohol and sulphurous acid. The water layer, if present, is removed by means of a separatory funnel. The ether is washed first with dilute caustic soda solution (?), then with small quantities of distilled water. The ether is now put into a glass stoppered bottle (?) and one half its weight of granular calcium chloride is added. The ether is allowed to stand for several days and then filtered into a clean, dry glass stoppered bottle. Save a small specimen. How could you prove the presence of ethylsulphuric acid in the flask in which ether was made?

Determine the boiling point, specific gravity, color, taste and odor. Is it a good solvent? Does water dissolve ether? Does ether dissolve water? Put 1 cc. of ether in an iron dish and ignite. What are the products of the combustion? Write out the equation. In a thin walled glass test tube put 3 cc. of water and place the tube in a small beaker containing ether. Blow air from the blast over the surface of the ether. What happens to the water in the test tube? Explain. Place a little ether on the hand and blow over it.

CAUTION.—*Never boil ether over a free flame; and in working with it, always carefully avoid the neighborhood of flames. In distilling it in a water bath, do not heat the water to boiling.*



EXPERIMENT 13

ALDEHYDE

Dissolve 5 grams of potassium bichromate in water and slowly add 15 cc. of conc. sulphuric acid. Is there any color change? Cool and add a few cubic centimeters of alcohol. Warm. Is there any color change? Note the odor. What is formed? How could it be obtained from the solution? What would be left in the solution? Write out the equations representing each step.

Obtain 50 cc. of *paraldehyde* from the stock room. Put it in a 150 cc. round bottom flask, *add 2 drops only* of conc. C.P. sulphuric acid and distil through a Hempel tube, keeping the temperature in the thermometer tube below 30°. Use the same type of receiver as was used for ether, and surround it with a freezing mixture (?). What distils over? Determine its boiling point, taste, odor, color and flammability. Compare the odor with that obtained when alcohol was warmed with the bichromate mixture. Is aldehyde lighter or heavier than water? Does it dissolve iodine and sulphur? Heat a few drops of the aldehyde with caustic potash solution, noting any change of color and odor. Explain. Save a small specimen of the aldehyde and use the remainder in the following experiments.

CAUTION. — *Aldehyde is very volatile and flammable; care must, therefore, be taken to avoid the presence of a free flame when working with it.*

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EXPERIMENT 14

ALDEHYDE AMMONIA

(Hood)

To 5 cc. of the aldehyde add 20 cc. of anhydrous ether, cool in a freezing mixture, and saturate with dry ammonia gas. (The latter is easily obtained, in case a tank of ammonia is not available, by heating a strong solution of ammonia and passing the evolved gas through an empty cylinder and then through a cylinder containing soda lime.) Note result and explain. Filter off the crystals, dry and save a specimen. More crystals may be obtained by evaporating the ethereal solution. Heat some of the aldehyde ammonia with dilute hydrochloric acid and note the odor. Explain.

EXPERIMENT 15

METALDEHYDE AND PARALDEHYDE

(Hood)

Cool 5 to 10 cc. of the aldehyde in a test tube in a freezing mixture, and pass in a few bubbles of *dry* hydrochloric acid gas. (The latter may be obtained by heating concentrated hydrochloric acid and drying the gas evolved by passing it through a wash bottle containing conc. sulphuric acid.) It is essential that the aldehyde, apparatus and hydrochloric acid gas should be absolutely dry. What happens? Explain. Filter off the crystals and dry them. Save a specimen. Cool the filtrate in a freezing mixture of crushed ice and conc. hydrochloric acid. Note result and explain. Save a specimen.

EXPERIMENT 16

DETECTION OF ALDEHYDE

To 10 cc. of an approximate N/10 silver nitrate solution, add cautiously drop by drop a *dilute* (3N) solution of ammonia, until the silver oxide first precipitated is *just* dissolved. Avoid *any* excess of ammonia. An ammoniacal solution of silver oxide is thus obtained.

Clean a test tube thoroughly by boiling some conc. nitric acid in it, pouring out the acid and washing with distilled water. Half fill the cleaned test tube with the ammoniacal silver oxide solution and add a drop of a dilute aqueous solution of aldehyde. Place the test tube in a beaker of cold water and heat the water in the beaker to boiling. Note the result and explain. This reaction is characteristic of the aldehyde group. What practical use is made of this reaction? What aldehyde is used? How delicate is this reaction as a test both for aldehyde and for silver?

See Roscoe and Schorlemmer's *Treatise on Chemistry*, vol. III, p. 478.

EXPERIMENT 17

FORMIC ACID

(Hood)

Into a 500 cc. dry distilling flask put 200 grams of crystallized oxalic acid and 200 grams of *anhydrous* glycerol (or "Glycerol Residues," see below). Insert a thermometer through the cork, so that the bulb dips below the surface of the glycerol, and connect the flask with a condenser and a receiver. Heat gently with a burner, keeping the temperature of the liquid between 100° – 115° . What gas is given off? When this gas ceases to be evolved, and after the contents of the flask have cooled to 75° , add 50 grams more of the crystallized oxalic acid, and heat as before. Repeat this addition of oxalic acid until 100 cc. of distillate have collected in the receiver. Put the glycerol into the bottle marked "Glycerol Residues," and set aside 25 cc. of the distillate for the experiments given below. Divide the rest into three portions. Neutralize one portion with chalk or slaked lime, filter, evaporate to crystallization, and save specimen of the calcium salt. Warm the second portion with a slight excess of lead carbonate or oxide, decant through a filter, and extract the precipitate two or three times with boiling water (?). Evaporate the combined filtrates to crystallization and save a specimen of the lead salt. Heat the third portion until saturated with freshly precipitated copper hydroxide (obtained by precipitating a solution of copper sulphate with caustic soda solution and washing the precipitate *thoroughly* with water), filter, evaporate the filtrate to crystallization, and save a specimen of the copper salt.

With the 25 cc. of the distillate perform the following experiments:—

- (a) Heat a small quantity with some mercuric oxide and note the result. Explain.

(b) Heat some with a solution of silver nitrate and describe and explain what takes place.

(Explain why these two reactions are characteristic of formic acid.)

How is formic acid made from chloroform?

Describe both the physical and chemical properties of the acid and all the salts made; save specimens of all the salts and of the distillate.

(Use the material in the bottle marked "Glycerol Residues" to start with, if it is available, instead of glycerol itself, and add only 50 grams of oxalic acid at a time.)

EXPERIMENT 18

ACETIC ACID

(Hood)

150 grams of *fused* sodium acetate are powdered and put into a 500 cc. dry distilling flask. The flask is cooled, and 180 grams of concentrated sulphuric acid (sp. gr. 1.842) are gradually added through a funnel tube reaching to the bottom of the flask. The flask is then connected with a condenser and receiver and heated. The distillate is subjected to fractional distillation, using a short Hempel distilling tube, or a distilling flask, with a column of glass balls in the neck (see figure), and an ebullator tube.

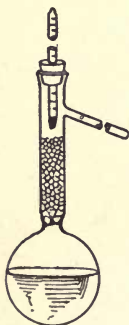
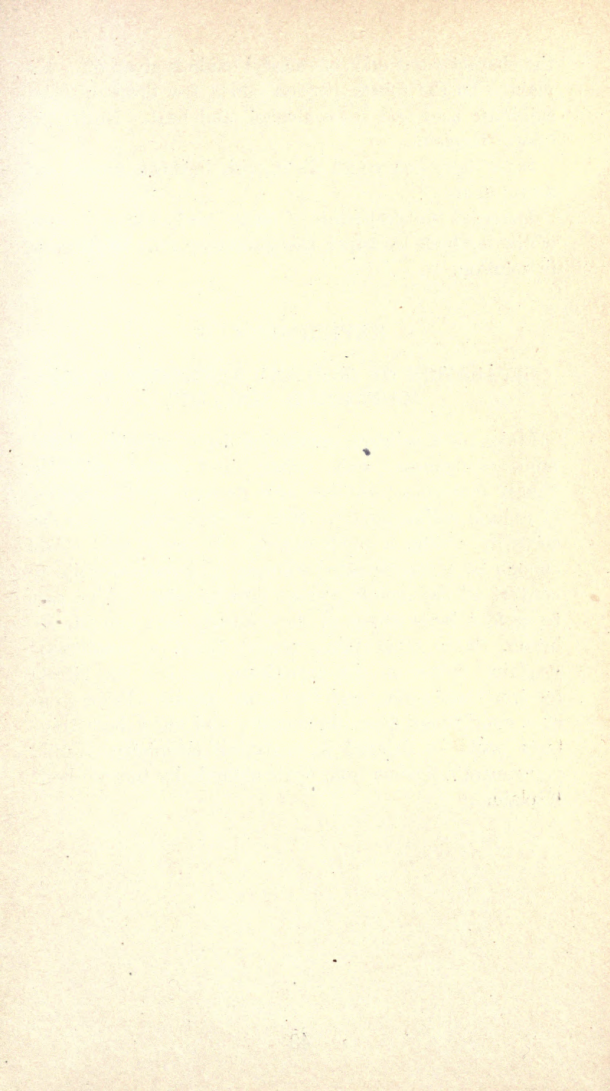


FIG. VII

First an aqueous acid passes over and is collected separately, but between 117° and 119° the anhydrous acid distils. Cool this distillate (between 117° – 119°) with ice water, and note what takes place. Save specimen of the glacial acid. Why is the first distillate not anhydrous?

A portion of the first distillate of the aqueous acid is *carefully* neutralized with caustic soda solution and divided into four portions. One portion is heated to boiling, and then a slight excess of mercurous nitrate solution added.

Explain what takes place. The second portion is also heated to boiling, and a tolerably concentrated solution of silver nitrate added. Note what takes place. Explain. The third portion is evaporated to dryness, on a steam or water bath, with some powdered arsenic trioxide, and a *little* of the resulting mass heated in a test tube when



the characteristic odor of cacodyl oxide is given off. Explain. To the fourth portion add a few drops of conc. sulphuric acid and some alcohol, and heat. Notice the odor. Explain.

Show how you could distinguish between formic and acetic acids.

Describe the properties of acetic acid, and give some of the methods by which this substance may be detected in solution.

EXPERIMENT 19

SEPARATION OF IRON AND ALUMINUM FROM MANGANESE, ZINC, ETC.

Make up a solution containing ferric chloride, aluminum, manganese, zinc, cobalt, and nickel chlorides. Nearly neutralize any free acid present with a solution of sodium carbonate (?). If a precipitate is formed dissolve by adding a small quantity of acetic acid. Add enough of a concentrated solution of sodium acetate to convert all the metals present into acetates (taking care to *avoid* a large excess of the reagent), and boil the solution. Note what takes place. What is volatilized? Explain. Filter off the precipitate and test the filtrate for iron, aluminum, and the other metals. Draw your own conclusions from the results, and show how these facts could be utilized in analytical chemistry. Could you separate ferrous from ferric chloride by this method? Explain.

EXPERIMENT 20

ACETYL CHLORIDE

(Hood)

20 grams of *glacial* acetic acid are put into a *dry* (?) 250 cc. round bottom flask, the flask cooled with ice water, and 30 grams of phosphorus trichloride (weigh this under the hood (?)) are gradually added, with constant shaking. Connect the flask with a return condenser, and heat it in a water bath to 50° – 60° C. until almost all the hydrochloric acid gas has been expelled. The condenser is then turned down and the acetyl chloride distilled off, care being taken to protect the distillate from the action of the moisture in the air by means of a tube containing calcium chloride. The distillate is then placed in a small, dry distilling flask, and redistilled with the same precautions as before. Note the boiling point.

What remains in the flask in which the acetyl chloride was made?

Determine the properties of acetyl chloride, including color, odor, and action on moist air.

Treat a few cubic centimeters of absolute alcohol with acetyl chloride and note what takes place. What gas is given off? What is formed? Explain. Repeat the experiment, using water instead of alcohol. Explain. What conclusions would you draw regarding the relation between water and alcohol from this experiment? What use is made of acetyl chloride in the laboratory?

EXPERIMENT 21

ACETIC ANHYDRIDE

(Hood)

20 grams of finely powdered anhydrous sodium acetate are placed in a dry 250 cc. distilling flask. A small separatory funnel is fitted into the flask and the flask is connected with a condenser, adapter and a suction flask as a receiver, the side arm being attached to a tube filled with calcium chloride (?). 15 grams of acetyl chloride are now added *slowly*, drop by drop, through the separatory funnel. If the acetyl chloride is added too fast it will distil over into the receiver unchanged. It should then be poured back into the separatory funnel and added more slowly. Shake constantly while adding the acetyl chloride. Then remove the separatory funnel, fit the flask with a cork and distil the anhydride. The distillate is freed from any acetyl chloride that may be present by distillation with 3 grams of finely powdered anhydrous sodium acetate and the boiling point of the anhydride is noted. Determine the physical properties of the anhydride. Save a specimen in a sealed tube.

To 5 cc. of water add a few drops of acetic anhydride. Note what happens. Warm the mixture and note what happens. Explain.

To 5 cc. of water and a few drops of the anhydride, add a little caustic soda solution. Shake, note what happens and explain.

To 2 cc. of alcohol add 1 cc. of the anhydride and heat gently for several minutes. Treat with water and make the solution slightly alkaline. Note the odor. What is the substance formed? Explain.

Compare the reactions with water and alcohol with the corresponding reactions with acetyl chloride.

What use is made of acetic anhydride in the laboratory?

EXPERIMENT 22

ETHYL ACETATE

(*Acetic Ether*)

Arrange an apparatus¹ like that used in the preparation of ether (see Experiment 12). Into the round bottom flask put 50 grams of conc. sulphuric acid and 50 grams of absolute alcohol (95% will do). Heat till the temperature reaches 130°-140° C., and then add gradually through the separatory funnel a mixture of 30 grams of glacial acetic acid and 30 grams of absolute alcohol (95% will do).

Separate the crude acetic ether from the water and wash with caustic soda solution; dehydrate in the usual manner with fused calcium chloride, and subject to fractional distillation.

Determine color, taste, odor, boiling point, specific gravity, solubility and flammability. Is there any analogy in the method of preparation of this acetic ether and the method used to make ordinary ether? What else is formed here besides acetic ether? Save a small specimen. Use 20 grams of the ethyl acetate in the following experiment.

¹Use a 1 liter flask.

EXPERIMENT 23

SAPONIFICATION

Calculate the amount of solid caustic soda necessary to decompose 20 grams of the ethyl acetate made in Experiment 22, assuming that the caustic soda contains 10 per cent of water. Dissolve this amount plus 5 grams excess in 300 cc. of water in a 500 cc. round bottom flask and add the 20 grams of ethyl acetate. Connect the flask with a reflux condenser and heat the mixture to boiling for one hour or until the odor of ethyl acetate has disappeared. Explain what takes place. Why is this process called saponification?

Then distil off 100 cc. of the liquid and examine the distillate. What does it contain and how is this shown?

Acidify the mixture in the flask *when cold* with dilute sulphuric acid and again distil. What passes over now? Does the distillate have an acid reaction? How could the amount of the substance present in the distillate be determined?

Given a mixture of ethyl acetate and ethyl alcohol explain how the amount of each could be determined.

EXPERIMENT 24

POTASSIUM CYANIDE¹

(Hood)

50 grams of potassium ferrocyanide are dehydrated by heating the powdered salt in a porcelain dish in an air bath at 110° until it ceases to lose weight. The dehydrated salt is powdered again and placed in an iron or copper retort provided with a cover, asbestos paper gasket, and an outlet tube. Exclude air from the retort by keeping the outlet tube under water. Protect the table top by means of a square of asbestos board placed on glass rods. Heat the retort to red heat with a good triple burner. A gas comes off; collect some and see if it will support combustion. Continue the heating until the gas ceases to be evolved. Then remove the outlet tube from the water and cool the retort. Take out the contents of the retort and grind in a mortar to a fine powder. Put the powder in a flask and extract twice with boiling methyl alcohol, using a reflux condenser and a water bath. Use 100 cc. of methyl alcohol for each extraction. Filter the alcoholic extracts while hot and allow them to cool. If crystals separate, filter them off and dry them. Otherwise, distil off some of the methyl alcohol until crystals do separate when the solution is cooled. Continue with the mother liquors until a maximum yield is obtained. Save a small specimen of the crystals.

Determine the solubility and the crystal form of the salt. Does it resemble potassium chloride in any way? Has it an odor? Explain. Is the salt deliquescent? Does the aqueous solution decompose on boiling? What is formed? Is the aqueous solution alkaline? Explain. Fuse some of the salt in a test tube with a little lead oxide (PbO). Note what happens and explain. Does an aqueous solution of the salt dissolve the cyanides of silver and gold? What use is made of this property?

¹ See Thorpe's *Dictionary of Applied Chemistry*, article on Cyanides.

Does an aqueous solution of the salt dissolve gold? Write the equation.

CAUTION.— *Potassium cyanide is extremely poisonous and great care must be taken in working with it. The hands should be thoroughly washed after handling the salt and the finger nails should be cleaned.*

Methyl alcohol is also poisonous and care must be taken not to breathe its vapor.

EXPERIMENT 25

POTASSIUM FERRICYANIDE

Dissolve 26 grams of crystallized potassium ferrocyanide in 200 cc. of distilled water, and add 8 cc. of concentrated hydrochloric acid. Into this solution drop slowly, from a separatory funnel, a solution of 2 grams of potassium permanganate in 300 cc. of distilled water. The reaction is complete when a drop of the solution added to a solution of ferric chloride gives a brownish red color but no precipitate. *If acid*, neutralize the excess of hydrochloric acid with chalk, filter, and evaporate on a water-bath to crystallization.

Save a specimen of the salt, and determine color, taste, crystal form, solubility, etc., of the potassium ferricyanide. Does the solution decompose in the light? What use is made of this salt?¹

Is it a good oxidizing agent? Try it in alkaline solution with some lead oxide. Does potassium ferrocyanide contain water of crystallization? Does the ferricyanide? To a small quantity of a saturated solution of the ferrocyanide in a test tube add an equal volume of fuming hydrochloric acid. Add two or three volumes of fuming hydrochloric acid to one volume of a saturated solution of the ferricyanide. Explain what takes place in each case.

¹ See Thorpe's *Dictionary of Applied Chemistry*, article on Photography, vol. IV, p. 231.

EXPERIMENT 26¹

POTASSIUM CYANATE

Mix intimately 100 grams of *dehydrated* powdered potassium ferrocyanide with 75 grams of *dry*² powdered potassium bichromate, which has been previously melted. A *little* of this mixture is placed in a porcelain or, better, an iron dish and heated (considerably below redness) until the mixture begins to glow and blackens. The rest of the mixture is then added *little by little*, each quantity being allowed to blacken before the next is added (complete oxidation of the cyanide to cyanate is thus effected). After cooling, the contents of the dish are extracted several times with boiling alcohol (450 cc. of 80% alcohol and 50 cc. of methyl alcohol). Filter, and cool the alcoholic solution to 0°. Filter off the crystals formed, using a Buchner funnel and suction pump. Dry on drying paper. *Continue the extraction until the black mass is exhausted.*

Save a small specimen of the cyanate. Determine crystal form, solubility, color, taste, odor, etc. Does the aqueous solution decompose on standing? What are the products? Add some dilute sulphuric acid to a solution of the cyanate, and explain what takes place. Is there any resemblance between potassium cyanate and potassium hypochlorite? Show this by the method of formation, one from cyanogen and the other from chlorine and a solution of potassium hydroxide. Prepare 20 grams of the cyanate and keep it for the preparation of urea, Experiment 42.

¹Read carefully the directions in the *Chemical News*, vol. 32, p. 99.

²Heat some in a test tube, and see that it gives off no water.

EXPERIMENT 27

POTASSIUM THIOCYANATE

An aqueous solution of 13 grams potassium cyanide is boiled with 6.4 grams flowers of sulphur in a round bottomed flask connected with a reflux condenser, until all the sulphur is dissolved. Filter the solution and evaporate to crystallization. Drain off the crystals and repeat the evaporation with the mother liquor.

Determine properties of the salt, including color, taste, odor, crystal form, solubility, and melting point. What takes place when the crystals are left exposed to the air? Is there any analogy between the formation of the cyanate (Experiment 26) and the thiocyanate? What use is made of the thiocyanate in the analytical laboratory? Heat some of the salt in a porcelain crucible and note the changes in color. Let cool and note any changes.

Save a specimen of the potassium salt.

Dissolve 5 grams of potassium thiocyanate in water, and note any change in the temperature of the water. Explain.

EXPERIMENT 28

AMMONIUM THIOCYANATE

Mix 60 grams of alcohol (95%), 80 grams of ammonia solution, and 35 to 40 grams of carbon bisulphide,¹ and allow to stand in a *glass stoppered bottle* until all the carbon bisulphide has dissolved. The process may be hastened by shaking the bottle from time to time, relieving any pressure by removing the stopper. When all the carbon bisulphide has dissolved, evaporate the solution at a gentle heat on a steam or water bath (Hood) to one third of the original volume. What goes off? Filter off any sulphur that may separate out, while the solution is hot. On cooling, ammonium thiocyanate crystallizes out. Filter off the crystals and repeat the evaporation with the mother liquor.

Determine crystal form, solubility, color, taste, odor, and melting point of the salt. How is thiourea made from ammonium thiocyanate?

Save a specimen of the salt.

EXPERIMENT 29

ALDEHYDE

(Hood)

Mix equal weights (1 gram) of dry calcium formate and dry calcium acetate. Distil from a test tube fitted with a delivery tube. Collect some of the distillate in water. What does the water contain? Prove it by making a silver mirror.

¹ Carbon bisulphide is very flammable. In working with it always avoid any flames.

EXPERIMENT 30

PALMITIC ACID, STEARIC ACID AND GLYCEROL

(Saponification of Fats)

Heat 10 grams of solid caustic soda in a small flask with 20 cc. of water until it is all in solution and add 150 cc. of alcohol. Melt in a porcelain dish on a water bath 10 grams of lard and then add to it the alcoholic solution of caustic soda. Evaporate to a syrupy consistency on a water bath, with constant stirring, and then allow the mass to cool. Convince yourself that the substance left is soap (?).

Is it a *hard* or a *soft* soap? Explain. How is a soft soap converted into a hard soap? Dissolve a *little* of the soap in water and filter if necessary. Divide the solution into three portions, and add to the first portion a few drops of a solution of calcium sulphate, to the second a few drops of a solution of magnesium sulphate, and to the third a few drops of a solution of calcium acid carbonate. Explain what happens in each case.

What is meant by the terms *permanent* and *temporary hardness* of water? How can the *hardness* of water be determined? How could a *hard* water be made soft?

Save a small specimen of the soap and *dissolve* the rest in a liter of hot water. Cool. Be sure that all of the soap is in solution and then acidify with dilute sulphuric acid. What is the precipitate formed? Filter off the precipitate, wash with water, dry and recrystallize it from alcohol. Prove that the substance is an acid. Save a specimen.

Neutralize the acid filtrate *exactly* with a solution of sodium hydroxide and evaporate it to dryness. Extract the residue with absolute alcohol several times *until it is exhausted*, filtering the alcoholic solutions. Combine the

alcoholic filtrates and distil off the alcohol, using a water bath. What is the syrup which remains?¹ Save a specimen.

Determine color, taste, odor, solubility of glycerol. Is it hygroscopic? Can it be distilled under ordinary pressure? What is its boiling point? Does glycerol dissolve caustic potash, lead oxide (PbO), or calcium oxide? Explain.

¹ In order to test the syrup for glycerol: Make a borax bead, and when cold moisten it with some of the syrup. Heat the bead in the flame of a Bunsen burner. If glycerol is present the flame will be colored green. Explain.

EXPERIMENT 31

OXALIC ACID

(Hood)

In a long necked flask, of about 1 liter capacity, heat gently 25¹ grams of cane sugar and 125 grams of conc. nitric acid. Gases are evolved. Explain. After the reaction is over, evaporate the solution to crystallization and let cool. Filter or pour off the mother liquor and add to it a smaller quantity of nitric acid, heat, and again evaporate to crystallization. Filter off the crystals, drain completely on a Buchner funnel and recrystallize from distilled water.

Determine color, taste (poison), odor, solubility, crystal form, etc., of the acid. Is it a strong acid? (See Experiment 41.) Does it contain water of crystallization? Prove it. Does it sublime when heated? Is it a reducing agent? Why? What does the acid yield when heated with glycerol? Neutralize a solution of oxalic acid with ammonia and add a solution of calcium chloride. What is formed? How is oxalic acid determined quantitatively?

What does oxalic acid give when heated with conc. sulphuric acid?

Dissolve some oxalic acid in water and add some dilute sulphuric acid (?). Now run in a little of a dilute solution of potassium permanganate and note what takes place. What becomes of the permanganate and of the oxalic acid? Write out the equation and calculate how much permanganate would be necessary to oxidize 5 grams of *crystallized* oxalic acid.

Save a specimen of oxalic acid. Write out equations after glucose has been considered.

¹ Since the action may be quite violent, it is best to put the sugar into the flask and clamp the flask under the hood exhaust before the acid is added.

EXPERIMENT 32

BASIC FERRIC SUCCINATE

Dissolve about a gram of succinic acid in water, and neutralize *carefully* with dilute ammonia solution. Add some of this solution of ammonium succinate to a neutral solution of manganese chloride and ferric chloride, and boil. A precipitate is formed. What is it? Filter it off, and test the filtrate for iron and for manganese, and draw your own conclusions from the results. Has the filtrate an acid reaction? Explain. Compare results with those obtained in Experiment 19.

EXPERIMENT 33

FEHLING'S SOLUTION

Dissolve 3.5 grams of crystallized copper sulphate in 50 cc. of distilled water. Bottle and label, "Copper Sulphate Solution." Dissolve 17.3 grams of Rochelle salt and 10 grams of anhydrous sodium carbonate in 50 cc. of water. Bottle and label, "Alkaline Tartrate Solution." For use mix equal volumes of the two solutions and dilute with an equal volume of distilled water.

Into a small porcelain dish put 5 cc. of each of the above solutions and add 10 cc. of distilled water. Heat nearly to boiling and add a few drops of a 1% solution of glucose. Note what takes place. Continue to add the glucose solution drop by drop until the precipitate settles and leaves the solution clear and colorless. Filter off the precipitate, wash with hot water, dry, and save specimen. What is this precipitate? What becomes of the glucose? Does a solution of glucose reduce an ammoniacal solution of silver oxide? Try it. What conclusions do you draw from these facts as to the constitution of glucose?

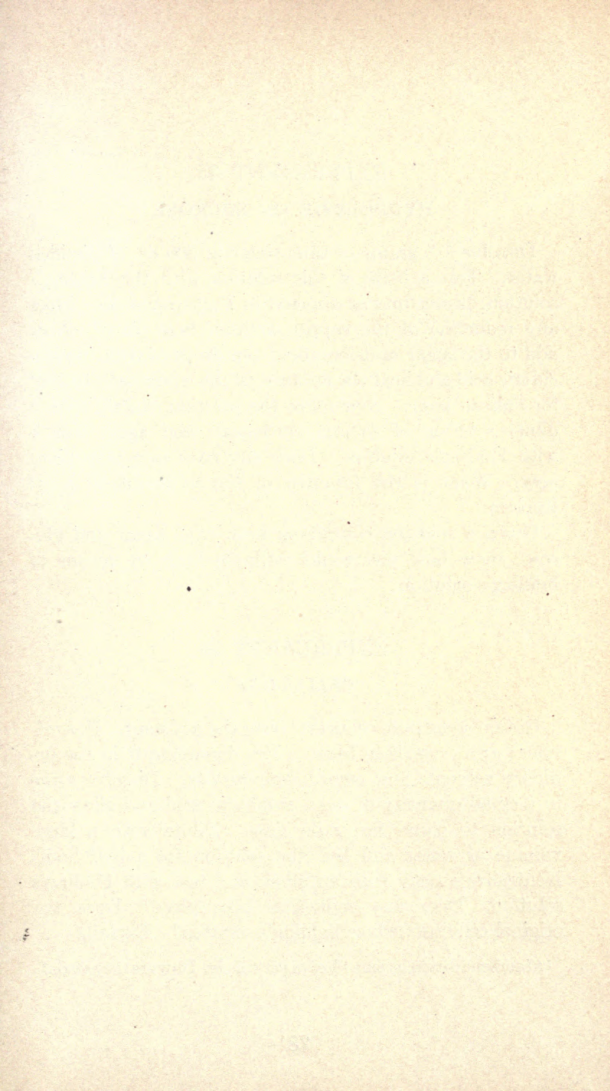
EXPERIMENT 34

PHENYLGLUCOSAZONE¹

Put 1 gram of pure glucose, 2 grams of pure phenyl hydrazine hydrochloride, 3 grams of crystallized sodium acetate and 20 cc. of distilled water in a small round bottom flask. Close the flask *loosely* with a cork to prevent evaporation and place it in a beaker half full of boiling water. Note the time that the flask is placed in the boiling water. Shake the flask occasionally, without removing it from the hot water, and note the time that elapses before the appearance of a precipitate. What color has the precipitate? Filter off the precipitate, wash with cold water and recrystallize from 50% alcohol. Determine the melting point of the *osazone*, heating the sulphuric acid in the Thiele tube rapidly.

Repeat the experiment, using fructose instead of glucose, noting the time that elapses between the immersion of the flask in the boiling water and the appearance of the precipitate. What color has the precipitate? Recrystallize the precipitate from 50% alcohol and determine its melting point. Is the osazone thus obtained identical with that made from glucose? Explain.

¹See Mulliken's *Identification of Pure Organic Compounds*, vol. I, pp. 30, 32.



EXPERIMENT 35

HYDROLYSIS OF SUCROSE

Dissolve 1.5 grams of cane sugar in 200 cc. of distilled water. Test a little of this solution with the Fehling's solution, proceeding as directed in Experiment 33. Does any reduction of the copper solution take place? Now add to the sugar solution about ten drops of conc. hydrochloric acid and heat the mixture on the water bath to 100° for half an hour. Neutralize the solution exactly with a dilute solution of sodium carbonate, and again test it with Fehling's solution. Does any reduction take place now? What is the function of the hydrochloric acid? Explain.

Given a solution containing both cane sugar and glucose, show how you could estimate both by means of Fehling's solution.

EXPERIMENT 36

CELLULOSE

Obtain some pure cellulose¹ from the assistant. Has cellulose any crystalline form? Try dissolving it in the ordinary solvents and record your results. Dissolve some in a small quantity of conc. sulphuric acid and allow the solution to stand for some time. Dilute with a large volume of water and boil the solution for a half hour. Neutralize *exactly* with an alkali and test with Fehling's solution. Does any reduction take place? Does the original cellulose reduce Fehling's solution? Explain.

¹ Absorbent cotton or pure filter paper will do. How are they made?

EXPERIMENT 37

CELLULOSE ACETATE

Put 20 cc. of *glacial* acetic acid, 6 cc. of acetic anhydride and 2 drops of conc. C. P. sulphuric acid in a small glass stoppered bottle. Shred into small pieces 0.5 gram of absorbent cotton and stir this thoroughly into the above solution. Stopper and let the mixture stand for several days or until a clear solution is obtained. Then pour this clear solution slowly into a beaker containing 500 cc. of water with vigorous stirring. Filter on a Buchner funnel and dry by pressing the mass between pieces of drying paper. What is it? Save a small specimen.

Allow about one half of the product to stand, in a small Erlenmeyer flask with 20 cc. of chloroform until it has completely dissolved. Then pour this clear solution upon a large watch glass and allow the chloroform to slowly evaporate. Then pour cold water over the film (?) and allow it to stand for a few minutes. Lift the edge of the film and carefully remove it from the glass. Dry.

Is the film flammable? For what purposes is it used? Try its solubility in alcohol and ether.

EXPERIMENT 38

SCHWEIZER'S REAGENT

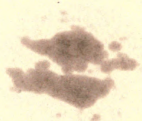
(Ammoniacal Solution of Copper Oxide)

To a mixture of 100 cc. of a conc. solution of ammonia and 30 cc. of water contained in a 250 cc. glass stoppered bottle add 5 grams of copper carbonate. Shake vigorously for a minute or two and then allow the mixture to stand for one hour, with occasional shaking. If a residue remains, decant the supernatant liquid or filter through glass wool and use the solution for the following experiments.

Does the above solution dissolve cellulose? Try it with some cotton cloth, filter paper and some absorbent cotton. Dilute the solutions thus obtained with water, filter them through glass wool (?), and acidify with dilute hydrochloric acid. What happens?

Explain the Willesden process for waterproofing cotton fabrics.¹ What is "Glanzstoff"?

¹See Thorpe's *Dictionary of Applied Chemistry*, under Cellulose.



EXPERIMENT 39

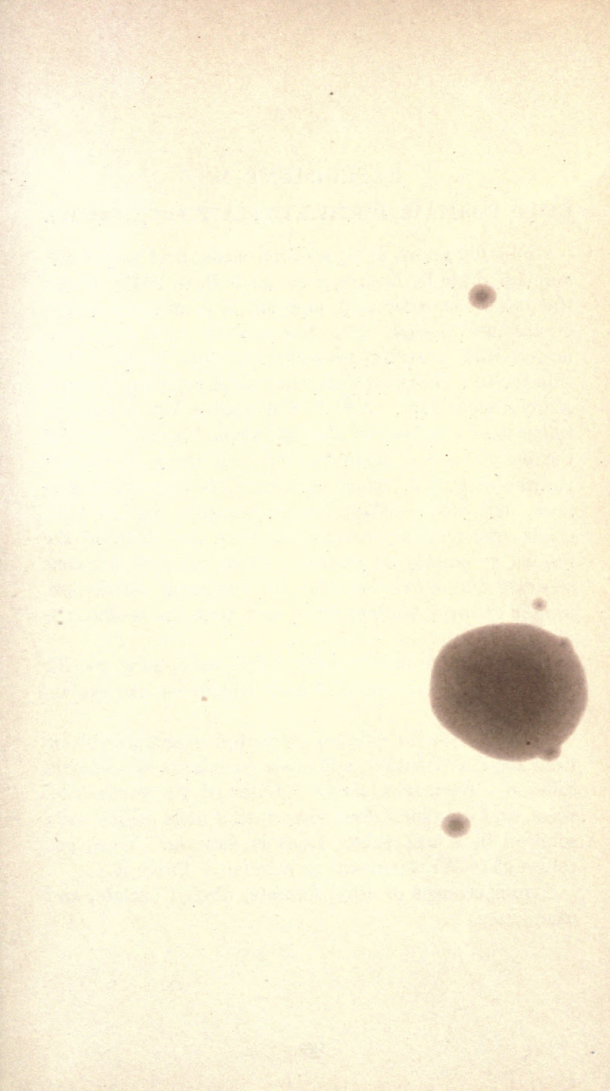
STARCH

Grind in a small mortar a gram of arrowroot starch with some distilled water. Pour the creamy mass thus produced slowly into 500 cc. of boiling distilled water contained in a porcelain dish, stirring constantly while the starch is being added so as to avoid the formation of lumps. A few drops of this solution is then added to a liter of water and *one drop* of a solution of potassium iodide. Does any color appear? Add a drop or two of freshly prepared (?) chlorine water and note what takes place. Explain. Is the color destroyed when chlorine water is added in excess? when alkalis are added? by sulphurous acid? by hydrogen sulphide? by sodium thio-sulphate? Try it with each reagent with a small quantity in a test tube. Explain and write out all equations. Does the color disappear on heating? Heat some in a test tube, and then cool. Does the color reappear on cooling? Explain. From the above conduct state whether the starch-iodine compound is a chemical compound or not. Test the delicacy of this reaction for iodine and for starch.

EXPERIMENT 40

HYDROLYSIS OF STARCH

Test some of the starch paste solution made in Experiment 39 with Fehling's solution. Does it reduce it? Add 5 cc. of concentrated hydrochloric acid to 200 cc. of the starch paste solution, and heat to boiling in a flask connected with a condenser for an hour and a half. When cold, neutralize with sodium carbonate solution, and examine with Fehling's solution. Does it reduce the Fehling's solution now? Does the solution now contain any starch? Test it with a solution of iodine in potassium iodide solution. Explain.



EXPERIMENT 41

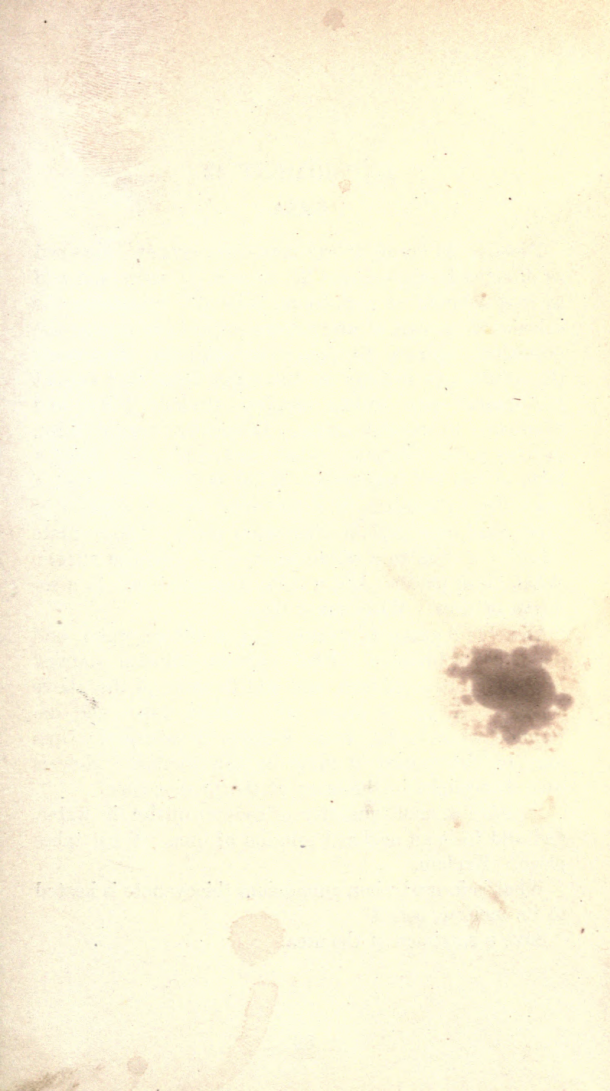
ETHYL FORMATE, DIETHYL OXALATE AND OXAMIDE

Grind 100 grams of crystallized oxalic acid to powder, and dehydrate by heating in an air bath to 100° . Weigh the *anhydrous* oxalic acid, and add to it an equal weight of absolute alcohol. Boil this mixture in a flask connected with a reflux condenser for four hours. Then transfer to a distilling flask, and distil until the temperature reaches 110° . Add to the residue left in the distilling flask a volume of absolute alcohol equal to that of the distillate, and again boil for four hours in the apparatus first used. Once more transfer to the distilling flask, and distil. When the temperature reaches 145° , change the receiver, increase the heat, and distil off the residue *as quickly as possible*. From the first fractions separate the ethyl formate, by fractional distillation, using a Hempel distilling tube, and, from the second, the diethyl oxalate.

Determine the boiling point, color, taste, odor, specific gravity, and flammability of both substances, and explain their formation.

To the alcoholic solution of diethyl oxalate, resulting from the fractionation, add some concentrated ammonia solution. What takes place? Filter off the precipitate, wash, and examine. Boil some with a little caustic soda solution in a test tube. Does it dissolve? What gas comes off? What remains in solution? Prove it.

Save specimens of ethyl formate, diethyl oxalate, and oxamide.



EXPERIMENT 42

UREA

Dissolve 20 grams of the potassium cyanate, obtained as directed in Experiment 26, in *cold* (?) water and add to it a solution of ammonium sulphate, containing the calculated amount of ammonium sulphate to change the potassium cyanate to potassium sulphate. Evaporate the solution to dryness on the water bath, and extract the residue with boiling absolute alcohol. Filter and evaporate to crystallization. Determine crystal form, melting point, solubility, color, taste, odor, etc. Heat a little of the dry substance. What is formed? Treat a concentrated solution in a test tube with a solution of oxalic acid, and explain what takes place. Add a dilute solution of urea to a dilute solution of mercuric nitrate. What takes place? Add a little mercuric oxide to a solution of urea. What takes place?

Dissolve 8 grams of caustic soda in 100 cc. water, and add 2 cc. of bromine. What does this solution contain? Make a solution of urea, and add to some of the above solution. A gas is given off. Collect some, and determine what it is. What remains in solution? Urea may be determined in urine by this method. How is urea determined in the urine at the present time?

Dissolve a small quantity of sodium nitrite in water, and add to it an acidified solution of urea. What takes place? Explain.

What is formed when ammonium thiocyanate is heated to its melting point?

Save a specimen of the urea.



EXPERIMENT 43

ETHYLENE AND ETHYLENE BROMIDE

Put 200 cc. conc. sulphuric acid, 100 cc. 95% alcohol and 10 grams of anhydrous aluminum sulphate¹ in a 500 cc. distilling flask. Close the flask with a cork carrying a thermometer the bulb of which dips below the surface of the liquid. Connect the flask with 3 Muencke gas washing bottles, the first containing water, the second 10 cc. of bromine² and 20 cc. of water and the third water only. Heat the flask to 138°–145°. What gas comes off? When the bromine has been decolorized (explain), separate the ethylene bromide from the water, using a separatory funnel, wash with dilute caustic soda solution, then with water, again separate from the water, dry with calcium chloride and distil, noting the boiling point.

Determine its color, taste, specific gravity (lighter or heavier than water), odor and solubility. Does it solidify on cooling? What is formed when it is treated in alcoholic solution with granulated zinc? How is ethylene alcohol (glycol) made from ethylene? Save a specimen of ethylene bromide.

¹ Made by calcining ammonium alum.

² Bromine should always be handled very carefully and under the hood.

EXPERIMENT 44

ALLYL ALCOHOL AND ACROLEIN

(Hood)

Put 200 grams glycerol and 70 grams of 85% formic acid in a 500 cc. distilling flask connected with a condenser, adapter and a suction flask as a receiver. Close the distilling flask with a cork carrying a thermometer, the bulb of which is immersed in the liquid. The side tube of the suction flask is connected with a gas washing bottle containing 30 cc. of water and surrounded with crushed ice. Heat the distilling flask (which is provided with an ebullator tube to prevent bumping) *rapidly*. The distillate up to 195° is collected separately and the heating is continued until the temperature reaches 260°, when it is stopped. The distillate between 195°–260° is saved. Allow the contents of the distilling flask to cool to 100° and then add 70 grams more of the 85% formic acid and repeat the distillation in the same manner as described above. The combined distillates (195°–260°) are treated with solid potassium carbonate, the allyl alcohol separated from the solution of potassium carbonate and distilled, collecting the distillate up to 103°. Heat this distillate with several grams of solid potassium carbonate, using a reflux condenser and separate the carbonate solution from the alcohol. Repeat this procedure until a fresh portion of the carbonate takes up no more water. Separate the alcohol from the carbonate and distil it, noting the boiling point.

Determine the odor, taste and solubility. Does it decolorize bromine water? Explain. Does it decolorize a *dilute* solution of potassium permanganate? Explain. Is allyl alcohol a primary alcohol? Save a specimen of the allyl alcohol.

Examine the water in the gas washing bottle. Note the odor. To what is it due? Does the solution reduce an ammoniacal solution of silver oxide? Prepare a silver mirror according to the directions given in Experiment 16. Save the mirror.

Does the solution decolorize bromine water? Does it decolorize a dilute solution of potassium permanganate? Explain.

EXPERIMENT 45

ACETYLENE

(Hood)

Put 5 grams of calcium carbide in a dry 500 cc. suction flask provided with a separatory funnel. The side tube of the suction flask is connected with a wide delivery tube and water is added through the separatory funnel *drop by drop*. Collect some of the gas in a test tube over water and see if it burns.

Pass some of the gas through a dilute solution of potassium permanganate contained in a test tube and note what happens. Explain. Pass some of the gas through an alcoholic solution of iodine in a test tube. What takes place? Explain. Show how acetic aldehyde, acetic acid, and ethyl alcohol could be acetylene.

Prepare 10 cc. of an ammoniacal solution of silver oxide (see Experiment 16) and pass the gas through it until the reaction is complete. A precipitate is formed. What is it? Filter it off, wash with water and examine. Determine color and solubility. Does it resemble silver chloride in any respect? Explain. Does it explode when heated or on percussion? Dry some *carefully* and try it. Save any silver solutions and put into bottle marked "Silver Residues." Destroy all of the silver of salt (?).

EXPERIMENT 46

BENZENE

Grind together intimately in a mortar 50 grams of benzoic acid and 100 grams of good soda-lime. Put the mixture in an iron retort, using an asbestos paper gasket. Connect the delivery tube of the retort with an adapter, and surround the receiver with ice water. Heat the retort with a triple burner, and continue the heating until liquid ceases to distil. Separate the oil from the water in the distillate, wash with dilute caustic soda solution (?), dry with fused calcium chloride, as usual, and redistil from a small distilling flask, noting the temperature at which it boils. What is the substance thus obtained?

Determine its specific gravity (lighter or heavier than water), odor, color, taste and flammability. Does it solidify when cooled to 0° ? Try it. Is it a good solvent? Try it. What remains in the retort in which this substance was made? Is there any analogy between this method of making benzene and the method of making marsh gas? Save a specimen of the benzene.



EXPERIMENT 47

NITROBENZENE¹

(Hood)

A cooled mixture of 60 grams of concentrated nitric acid and 80 grams of ordinary concentrated sulphuric acid is slowly and carefully added from a separatory funnel drop by drop, and with constant shaking, to 50 grams of benzene, contained in a $\frac{1}{2}$ liter flask, care being taken to prevent the temperature rising above 50°. Gases come off. What are they? Explain. When all the acid has been added, heat the mixture on a boiling water or steam bath for half an hour, shaking the flask constantly. After cooling, pour the mixture into half a liter of cold water, and separate the acid layer by means of a separatory funnel. Wash the oil remaining several times with water, and then with dilute soda solution, drawing off the oil each time from the *bottom* of the funnel. Wash finally with water, separate the oil from the water as completely as possible, dry with calcium chloride in the usual way, and subject to distillation, using a plain tube as a condenser and noting the boiling point. What comes over? What is the brownish residue left in the flask? Determine the specific gravity, solubility, color, taste and odor. Does it solidify on cooling? Why is the sulphuric acid added in the preparation of the nitrobenzene?

Save a small specimen of the substance, and use the rest in the following experiment.

¹The vapor of nitrobenzene is poisonous, and care should be taken not to inhale it.

EXPERIMENT 48

DINITROBENZENE

(Hood)

15 grams of nitrobenzene are gradually added from a separatory funnel to a mixture of 25 grams of concentrated nitric acid and 40 grams of concentrated sulphuric acid, contained in a flask of 500 cc. capacity. The flask should not be cooled, but should be frequently shaken during the addition of the nitrobenzene. When all the nitrobenzene has been added, heat the flask gently until red fumes cease to be given off and the reaction is complete. The flask should be shaken constantly during the heating. After cooling, pour *slowly* into a liter of water. Filter off the crystals on a Buchner funnel, using a suction pump to drain thoroughly, wash free from acid, drain, and recrystallize from hot alcohol.

Determine the melting point, crystal form, solubility, color, odor and taste of the crystals. What substances remain in the alcoholic mother liquor? Save a specimen of the crystals.

EXPERIMENT 49

ANILINE

Put 150 cc. of water, 55 grams of finely divided cast iron filings, and 40 grams of nitrobenzene into a 1500 cc. round bottom flask connected with a reflux condenser. Add 20 grams of concentrated hydrochloric acid through the inner tube of the condenser. Heat gently with a small flame until the reaction begins. After the first violent reaction is over, heat the contents of the flask to boiling and continue until the odor of nitrobenzene has disappeared (about 10 hours). Then add water (250 cc.) to the flask, and distil with steam. If the distillate has the odor of nitrobenzene and a little of the oil is not *completely* soluble in conc. hydrochloric acid, add conc. hydrochloric acid until the aniline has entirely dissolved and extract the nitrobenzene by shaking with ether. Then remove the ether, concentrate the aqueous solution, and add caustic soda solution to alkaline reaction, put into a separatory funnel, and extract two or three times with small quantities of ether. If the distillate does not smell of nitrobenzene, and a little of the oil dissolves *completely* in hydrochloric acid, simply extract it once or twice with ether. Separate the ether extracts from the water as completely as possible, dry with solid caustic soda, place in a distilling flask, and distil off the ether (with *care*). Finally, increase the heat, and distil the aniline. Determine its boiling point, solubility, specific gravity (lighter or heavier than water), color, odor, and taste. Has the solution in water an alkaline reaction? Try it. Does aniline dissolve in dilute acids? Explain. Is it affected by the light? Does its aqueous solution precipitate salts of zinc, aluminum, and iron? Try it.

Explain. Does aniline decompose ammonium salts? Heat some with ammonium chloride. Is ammonia given off?

Save a small specimen of aniline.

To a dilute aqueous solution of some of the aniline add an excess of a filtered solution of bleaching-powder, and note the result. Explain. *Very* dilute solutions of aniline give but a slight coloration, but a color is brought out by adding a few drops of a dilute solution of ammonium sulphide to the mixture. Try it, and test the delicacy of this last reaction.

To a solution of aniline in concentrated sulphuric acid add a few grains of solid potassium bichromate, and warm the test tube gently. What takes place?

EXPERIMENT 50

PHENYL ISOCYANIDE

(Hood)

Dissolve a small quantity of solid caustic potash in alcohol in a test tube and add one or two drops of aniline. Then add a drop of chloroform to 100 cc. of distilled water in a small flask, and shake the mixture thoroughly. Now add a drop or two of this water saturated with chloroform to the caustic potash solution containing the aniline, and heat the test tube *under the hood*. The odor is that of phenyl isocyanide.

This reaction is a very delicate one, and may be used to detect the presence of any primary amine or of chloroform. Is aniline an amine? What is the object of the caustic potash?

EXPERIMENT 51

m-NITROANILINE

Dissolve 5 grams of *pure* dinitrobenzene in 20 grams of alcohol in a 250 cc. Erlenmeyer flask. The solution is cooled; a portion of the dinitrobenzene separates. Then add 4 grams of conc. ammonia solution. The flask is then weighed, the weight noted and the mixture saturated with hydrogen sulphide (Hood), at room temperature. The flask is then connected with a reflux condenser and the solution heated on a water bath for a half hour. Cool, saturate again with hydrogen sulphide and then reflux as before. Continue this operation until there has been 3 grams increase in weight. The mixture is then diluted with water, the precipitate is filtered off and washed with water. It is then extracted several times with warm, dilute hydrochloric acid and the solution filtered. The nitroaniline is set free from the combined acid filtrates by neutralizing with ammonium hydroxide and recrystallized from hot water.

Determine melting point and color.

How is this substance made on the large scale? How could both nitro groups in dinitrobenzene be reduced? What is the product called?

EXPERIMENT 52

ACETANILIDE

(Hood)

To 5 cc. of aniline add acetyl chloride (about 5 cc.), drop by drop, through a small separatory funnel, waiting between each drop until the vigorous action ceases. When no action takes place upon the addition of a drop of the acetyl chloride the reaction is complete. Pour the mixture into five times its volume of water, shake and allow it to stand for a few minutes. What is the solid which separates? Recrystallize it from hot water and determine its melting point. What does it give when hydrolyzed with solutions of the alkalies?

For what purpose is acetanilide used? What effect has the introduction of the acetyl group into the aniline molecules on the toxicity?

EXPERIMENT 53

BENZENE DIAZONIUM CHLORIDE

Suspend 10 grams of powdered aniline hydrochloride in 30 grams of *glacial* acetic acid and 15 cc. of absolute alcohol, cool below 8° and add, *with constant shaking and slowly*, 10 grams of amyl nitrite,¹ taking care that the temperature does not rise above 8° . The suspended aniline hydrochloride quickly dissolves and the *diazotization* is complete when a small portion of the mixture, removed with a pipette, no longer gives a yellow color when treated with a solution of sodium acetate (?). Then treat with an equal volume of ether, keeping the temperature below 0° . Filter off the crystals of the diazonium chloride

¹ Do not breathe the vapor of amyl nitrite.

on a Buchner funnel by suction, wash with a little ether, and dry in the air on drying paper.¹ -

Determine the color, solubility, and crystal form of the salt. Does it decompose on standing in the light? Does it act like a substituted ammonium salt towards solutions of platinum chloride and gold chloride? Does it give a perbromide with a solution of bromine in potassium bromide? Does NH_4Br form a perbromide?

(a) Heat some of the dry salt *cautiously* on platinum foil, and note what takes place. Does the salt explode on percussion? Try it

(b) Boil some with absolute alcohol, and describe what takes place. What are the products of the reaction?

(c) Boil a little of the dry salt with water. What takes place? What are the products of the reaction? Prove it.

(d) Treat a cold solution of dimethylaniline in water with a cold aqueous solution of benzene diazonium chloride and observe what takes place. Explain.

(e) Treat a *cold* solution of phenol in water with a *cold* aqueous solution of benzene diazonium chloride and make the solution alkaline with sodium carbonate solution and note what takes place. Explain.

¹ The *dry salt* is *very explosive*, and great care must be exercised in handling it. Perform the whole experiment in one period and wash out all vessels containing the salt at once with water and use up all of the material before leaving the laboratory.

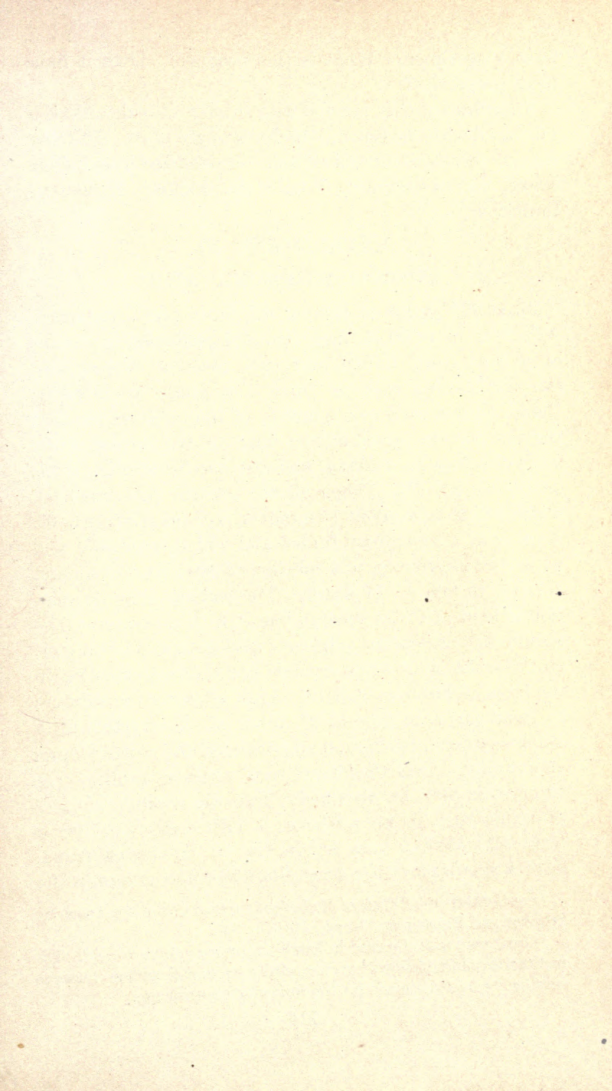
EXPERIMENT 54

IODOBENZENE, IODOBENZENE DICHLORIDE, AND IODOSOBENZENE

Dissolve 10 grams of freshly distilled aniline in a mixture of 50 grams conc. hydrochloric acid and 150 cc. of water in a 500 cc. Erlenmeyer flask. Cool the mixture with ice water below 8° and add gradually, *with constant shaking*, a cold solution of 9 grams of sodium nitrite in 50 cc. of water, until an *excess* of nitrous acid is shown to be present by the blue color a drop of the solution imparts to starch-potassium-iodide paper. Explain. What does this solution now contain? *When the diazotization is complete* (?) transfer the solution to a 2 liter balloon flask, cool to 8° and add a solution of 18 grams of potassium iodide in 40 cc. of water and allow the mixture to stand for about 2 hours at about 8° . Then heat it gently on the water or steam bath until the evolution of nitrogen ceases. Explain what takes place. Make the liquid strongly alkaline with caustic soda solution (?), distil off the oil with steam, separate it from the water by means of a separatory funnel, dry with calcium chloride, and redistil it, noting the boiling point. What is the substance thus obtained? Determine the color, odor, action of light, solubility and specific gravity (lighter or heavier than water) of the liquid. Save a specimen.

Dissolve some of the iodobenzene in five times its volume of chloroform, and saturate the solution with *dry* chlorine, using a wide delivery tube and keeping the solution cold by surrounding it with a freezing mixture. Filter off the crystals formed and dry them in the air on drying paper. Save a small specimen. What is this compound? Does iodine have basic properties?

Triturate the rest of the crystals obtained above with a dilute solution of caustic soda (for each gram of the crystals, use 0.5 gram sodium hydroxide in 4 grams of water) and allow the mixture to stand over night. Filter off the crystals, wash with water and dry on drying paper.



Save a specimen. What is this product? Does it have basic properties?

The filtrate is then treated with sulphur dioxide until it is saturated with the gas and smells strongly of it. The precipitate formed is filtered off and recrystallized from boiling water. Save a specimen. What is the product? Explain its formation.¹

EXPERIMENT 55

BENZENE SULPHONIC ACID²

Place 300 grams of fuming sulphuric acid (containing 20% SO_3) in a 500 cc. flask and add *gradually*, by means of a separatory funnel and *with constant shaking and thorough cooling with ice water* 100 grams of benzene. Before adding each new quantity of the benzene, see that the last portion, which at first floats on the surface of the acid, dissolves on shaking, and *keep the temperature of the acid below 50° (?)*. When all the benzene has dissolved, which will require about 15 minutes, cool the mixture to 0°, place it in a separatory funnel and add it, *gradually* and *with constant stirring*, to a solution of 200 grams of sodium chloride in 800 cc. of water. The sodium chloride solution is kept at 0° by surrounding it with ice water. The sodium salt of benzene sulphonic acid separates at once or, on the addition of a few crystals and thorough stirring, in the form of lustrous leaflets. After allowing the mixture to *stand for some time at 0°*, filter off the crystals on a Buchner funnel by suction and drain off the mother liquor thoroughly. Cool the filtrate to 0° again as another crop of crystals may be obtained. Dry the sodium salt in a porcelain dish in an air-bath at 110°. Recrystallize it from 95% alcohol and dry in the air on drying paper. Save a specimen of the crystallized salt and determine its

¹ See Gatterman's *Practical Methods of Organic Chemistry*, trans. by Schober and Babasinian, 3d ed., 1916, p. 246.

² Great care must be used in handling fuming sulphuric acid. Directions should be followed very carefully, as enough sodium benzene sulphonate must be made for the following experiments.

color, crystal form and solubility. Does it contain water of crystallization? Use the dry salt in the following experiments.

EXPERIMENT 56

BENZENE SULPHONYL CHLORIDE AND BENZENE SULPHONAMIDE

(Hood)

Grind together in a porcelain dish equivalent quantities (20 grams) of dry sodium benzene sulphonate (dried at 110°) and phosphorus pentachloride (24 grams).¹ What is formed? Then, after cooling, add 300 grams of ice and water with stirring. When the ice has melted extract the oil with 300 cc. of ether. Separate the ethereal solution from the water, dry with calcium chloride and distil off the ether, using a water bath and observing the usual precautions. What remains in the distilling flask? Save a small specimen and to the rest add 100 cc. of conc. ammonia solution, with constant stirring, and evaporate to dryness on a water bath. What is formed? Recrystallize the product from hot water, and determine its melting point, crystal form, solubility, color, taste and odor. Does the substance dissolve more readily in ammonia solution than in water? Explain. Save a specimen.

¹ If a good hood is not available, grind the materials together out of doors.

EXPERIMENT 57

PHENYL CYANIDE (BENZONITRILE) AND BENZOIC ACID (Hood)

Grind together intimately 40 grams of crystallized sodium benzene sulphonate and 12 grams of sodium cyanide, and distil the mixture from an iron or copper retort, the delivery tube of which is connected with a suction flask as a receiver by means of an adapter. What substance distils? Has it a bad odor? What remains in the retort? Prove it. Save a small specimen of the oil. How is phenyl cyanide made from aniline? Compare the odors of phenyl cyanide and phenyl isocyanide (Experiment 50). Put the rest of the oil in a 500 cc. flask, add 150 cc. of strong caustic soda solution, connect the flask with a reflux condenser, and boil the contents until the oil disappears. What is formed? What gas is given off? After cooling, acidify the solution with hydrochloric acid. Filter off the precipitate and recrystallize it from hot water. Determine its melting point and properties (see Experiment 62). Save a specimen.

EXPERIMENT 58

PHENOL FROM SODIUM BENZENE SULPHONATE¹

Dissolve 40 grams of sodium benzene sulphonate in as small a quantity of hot water as possible in an iron crucible and add 40 grams of solid caustic soda. Heat the crucible with a flame till all the water is driven off and then raise the temperature to 325° – 350° and continue the heating at this temperature for one hour with constant stirring. The temperature is taken with a thermometer fastened by means of a cork in a thin iron tube closed at one end, which is also used as a stirrer. The hand must be protected by a glove and goggles worn during the fusion. When cold dissolve the fused mass in the crucible by heating with several portions of water. Acidify the solution with hydrochloric acid. What gas is given off? Extract the oil with several portions of ether, dehydrate the ethereal extract with potassium carbonate and distil off the ether, observing the usual precautions. Then increase the heat and distil off the oil, noting its boiling point. Determine odor, color, crystal form, melting point and solubility. Save a specimen and perform the experiments (1, 2 and 3) given in Experiment 59.

¹ Do not allow phenol to come into contact with the skin. It produces painful and serious burns.

EXPERIMENT 59

PHENOL FROM ANILINE

Carefully add 20 grams of conc. sulphuric acid to 50 grams of water. While still hot add 10 grams of *freshly distilled aniline*, allowing it to flow down the sides of the beaker slowly while stirring the solution vigorously. Then add 100 cc. of water. Cool by surrounding the beaker with a freezing mixture. When the temperature is about 0° , add slowly and with constant stirring a solution of 9 grams of sodium nitrite in 50 cc. of water, keeping the temperature below 8° and testing for excess nitrous acid with starch-potassium-iodide paper. Let the mixture stand until the diazotization is complete. It is then gently heated for a half hour at 40° – 50° in a water bath. What gas is given off? The solution is then subjected to steam distillation until all the phenol has distilled over (?). The distillate is saturated with salt and extracted several times with ether. The ethereal extract is then dried with potassium carbonate, decanted or filtered into a small, dry distilling flask and the ether distilled off with the usual precautions.

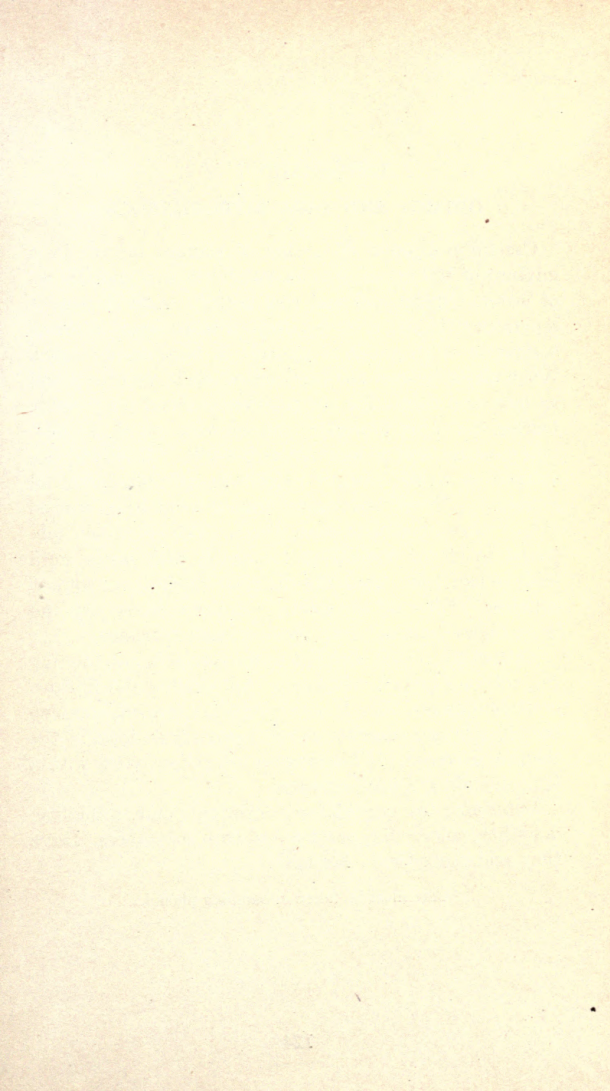
What remains in the distilling flask? Save a small specimen. Determine odor, color, crystal form, boiling point and solubility. Is the substance poisonous? What is its common name? Make a solution of it in water and perform the following experiments:

- 1: To a small portion of the solution add a few drops of a ferric chloride solution.

2. To another portion of the solution add $\frac{1}{4}$ volume of ammonia solution, and then a few drops of a solution of bleaching powder (1 part to 20 of water).

3. Add a few drops of bromine water to a third portion of the solution.

Describe what takes place in each case.



EXPERIMENT 60

ORTHO- AND PARA-NITROPHENOLS

Carefully dissolve 80 grams of sodium nitrate in a mixture of 100 grams of conc. sulphuric acid and 200 cc. of water. Shake well and cool to 25°. Add through a separatory funnel, drop by drop, with constant shaking, a solution of 50 grams of phenol¹ in 5 grams of alcohol. When all the phenol has been added shake well for a half an hour and then allow the solution to stand for 2 hours. During the entire procedure the temperature of the solution must be kept as near 25° as possible. Then add two volumes of water; a heavy reddish-brown transparent oil separates. The oil is separated from the water and washed two or three times with fresh water. The oil is then subjected to steam distillation (cover oil with water until flask is half full), until the distillate passes over almost colorless. Filter off the solid (?) in the receiver, dry and recrystallize from alcohol. Save a small specimen.

Extract the oil left with hot water several times, filtering the aqueous extract while hot. On cooling the filtrates crystals separate (?). If no crystals are formed, combine the filtrates and concentrate until crystals do form as the solution is cooled. If the crystals are yellow, wash with a *little ice water* (?), until colorless.

Determine the crystal form, melting point, solubility, volatility, color, odor, and taste of both substances. Have they acid properties? Explain.

¹Care must be taken in handling phenol.

EXPERIMENT 61

PICRIC ACID

(Hood)

Heat together in a round bottom $\frac{1}{2}$ liter flask to 100° a mixture of 20 grams of phenol and 20 grams of concentrated sulphuric acid until *complete* solution takes place.¹ What is formed? Remove the burner, dilute with twice the volume of water, and add the solution (from a separatory funnel and with constant shaking), *gradually and carefully*, to 100 grams of conc. nitric acid. Warm the mixture on the water bath until the red color changes to yellow, then pour into a liter of water, filter off the crystals on a Buchner funnel, drain thoroughly, wash with water, and purify by recrystallization from hot water containing 0.1% sulphuric acid.

Determine color, odor, taste (poison), crystal form, melting point and solubility of the compound.

Does an aqueous solution of the acid dye silk or wool permanently? Save specimens of the dyed cloth. Saturate some of the picric acid with a solution of sodium carbonate, and add to the hot filtered solution a few crystals of sodium carbonate. What takes place? Explain. Does phenol react with a solution of sodium carbonate? Does the dry sodium salt or the acid explode when heated or struck with a hammer? Save specimens of both the acid and the sodium salt, and write out all reactions.

¹ A sample taken out of the mass should be completely soluble in water.

EXPERIMENT 62

BENZYL ALCOHOL AND BENZOIC ACID FROM BENZALDEHYDE

Shake 20 grams of benzaldehyde in a cork stoppered bottle with a cold solution of 18 grams of potassium hydroxide in 12 grams of water until a permanent emulsion is formed and allow the mixture to stand over night. Add water until the pasty mass of crystals goes into solution and extract the benzyl alcohol from the clear solution by shaking several times with ether. Distil off the ether, observing the usual precautions, and then distil the alcohol, noting the boiling point. Determine its color, odor, solubility and taste. Is it a primary alcohol? Add hydrochloric acid in excess to the alkaline solution and recrystallize the precipitate from hot water. Compare it with the benzoic acid obtained in Experiments 57 and 63. How do acetic and formic aldehydes react when treated with alkalies? Save specimens of benzyl alcohol and of benzoic acid. Use the rest of the benzoic acid together with that obtained in Experiment 63 in Experiment 64.

Show how benzyl benzoate could be made by the Baumann-Schotten reaction. How is cinnamic acid made from benzaldehyde (Perkin's synthesis)?

EXPERIMENT 63

BENZOIC ACID

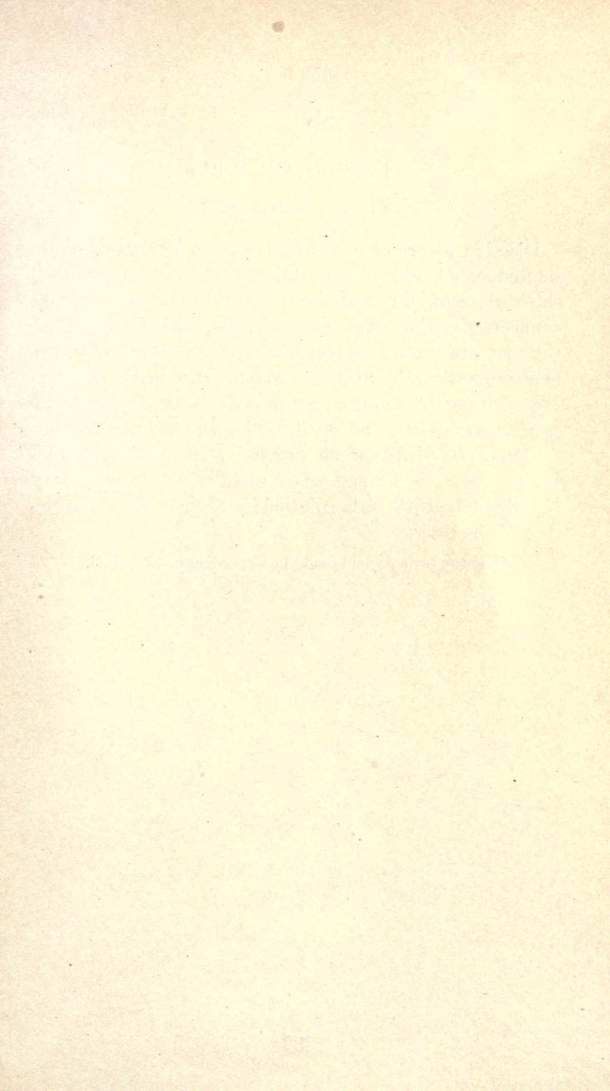
(Hood)

Boil 10 grams of benzyl chloride (in a 500 cc. retort with neck directed *upwards*), with a mixture of 30 grams of conc. nitric acid and 20 grams of water until completely oxidized (about ten hours). When the odor of benzyl chloride has disappeared, and no oil separates out on cooling, let the contents of the retort cool, and filter off the crystals. If the crystals are colored, decolorize them by boiling the aqueous solution with boneblack, or by recrystallization from boiling dilute nitric acid. What is this substance thus obtained? By what other methods have you already prepared it? Determine its melting point, odor, taste, crystal form and solubility. Is it volatile with steam?

Sublime a small amount of the benzoic acid as follows: Put a little into the bulb of a straight calcium chloride tube, heat until the acid melts and then pass a slow current of air through the tube. The length of the tube is increased by wrapping a piece of paper around it and fastening it with a rubber band. The vapors condense on the paper.

Save specimens of the crystallized and the sublimed benzoic acid.

How is benzoic acid made on the large scale?



EXPERIMENT 64

ETHYL BENZOATE

Dissolve 25 grams of benzoic acid ¹ in 100 grams of absolute alcohol, add to the solution 5 grams of concentrated sulphuric acid, and heat the mixture to boiling in a flask connected with a reflux condenser for three hours. Pour the contents of the flask into five times its volume of water, neutralize the acid with dry sodium carbonate, separate the oil from the solution, wash with water, dry with potassium carbonate, and distil, noting the boiling point.

Determine color, specific gravity, odor, taste and solubility. What is formed when some of the substance is boiled with caustic soda solution? Try it. Save a specimen of the ester.

¹ Use the benzoic acid made in Experiments 62 and 63.

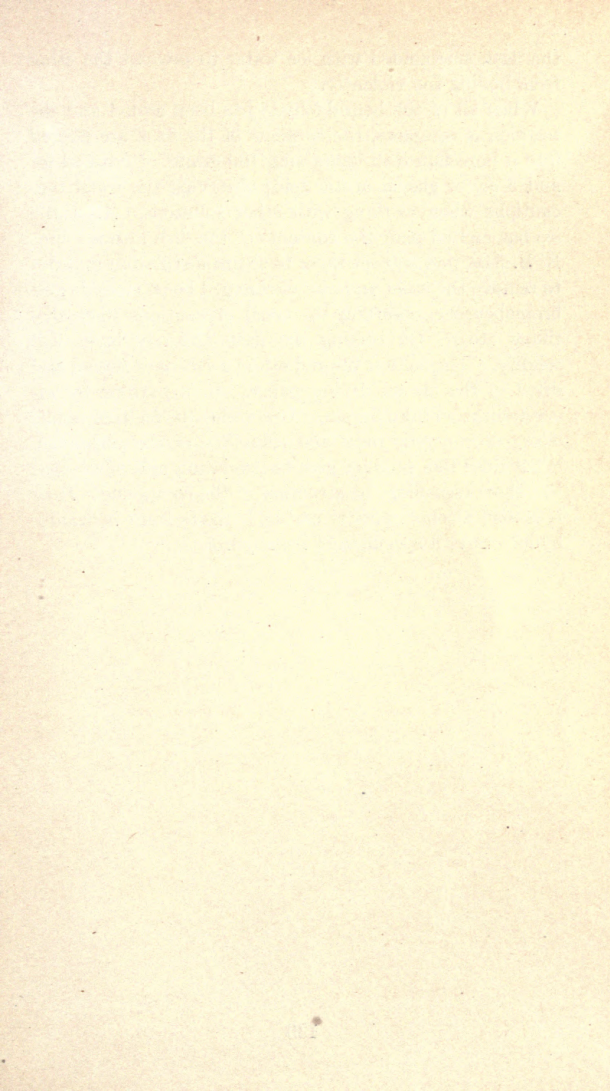
EXPERIMENT 65

GRIGNARD'S REACTION BENZHYDROL

(*Diphenyl Carbinol*)

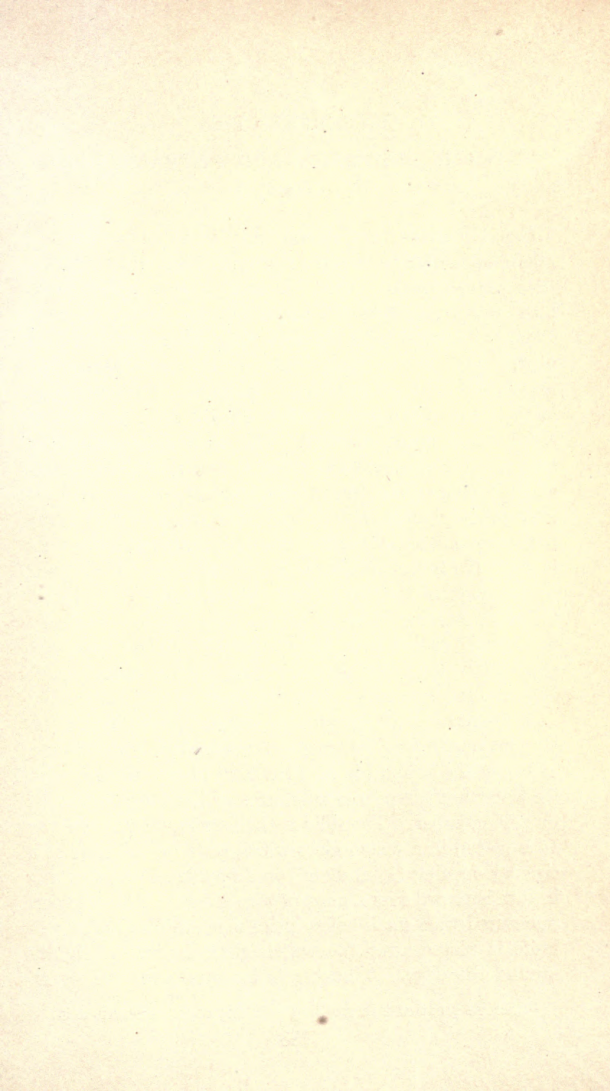
2.4 grams (1 mol.) of magnesium turnings and a small crystal of iodine are placed in a *dry* 250 cc. R. B. flask and warmed gently over a free flame until the color of the iodine vapor becomes visible in the flask. 17.2 grams (1.1 mol.) of *pure, dry* bromobenzene dissolved in 50 cc. of *absolute* ether (dried over sodium) are then added and the flask is connected with a reflux condenser, the inner tube of which must be *dry* and *clean*. A small calcium chloride tube containing calcium chloride and soda-lime is fitted by means of a cork to the upper end of this tube in order to protect the contents of the flask from the carbon dioxide and moisture of the air.

The flask is dipped into warm water (about 50°) until the reaction starts and the ether begins to boil, after which it is removed, as the heat of the reaction is sufficient to keep the ether boiling. When the ether has ceased boiling, the flask is heated in a water bath to the boiling point of the ether until all of the magnesium has dissolved. What substance is present in the ether solution? If a dark colored precipitate forms it is due to impurities in the magnesium. The flask is now *cooled in ice water* and a mixture of 10.6 grams (1 mol.) of *freshly distilled* pure benzaldehyde and 50 cc. of absolute ether is added *slowly, drop by drop*, from a separatory funnel inserted in the inner tube of the condenser in place of the cork and the calcium chloride tube. The flask is gently shaken after the addition of *each drop* of the solution of the benzaldehyde and no more of the solution is added until the first violent reaction is over. Care must also be taken to keep



the flask surrounded with ice water to prevent the ether from boiling too violently.

When all of the benzaldehyde has been added and the reaction is complete, the contents of the flask are poured into a porcelain dish containing 100 grams of crushed ice and 5 cc. of glacial acetic acid; observing the usual precautions when working with ether solutions. After the ice has melted pour the contents of the dish into a 1 liter R. B. flask and subject them to steam distillation in order to remove the ether and any unchanged benzaldehyde and bromobenzene, observing the usual precautions when distilling ether. On cooling the flask the oily layer will solidify. The solid is filtered off on a Buchner funnel and dried in the air on drying paper. It is purified by recrystallization from ligroin. Determine the melting point, odor, color, crystal form and solubility of the substance. What does this product give on oxidation and what does this show regarding the structure of the compound? How is benzyl alcohol (phenyl carbinol) made from benzaldehyde? Save a specimen of benzhydrol.



EXPERIMENT 66

PHTHALIC ANHYDRIDE AND PHTHALIC ACID

(Hood),

Grind together in a mortar until thoroughly mixed 50 grams of naphthalene and 13 grams of mercuric sulphate (or mercuric oxide). Put this mixture in a 1 liter tubulated retort and add 375 grams of conc. sulphuric acid. Clamp the retort with the neck turned upward and heat gently¹ over a wire gauze until all the naphthalene has dissolved (about 30 minutes). Explain. Turn the neck of the retort down and insert it tightly into the neck of a tubulated retort receiver. The opening (tubulure) of this receiver is connected with a cork and glass tubing which should extend to the hood exhaust, and the receiver is surrounded with cracked ice. The retort is then *gently* heated with a small moving luminous flame and the heat is *gradually* increased as needles of the anhydride appear in the neck of the retort and the sulphuric acid distils. Continue heating until as much as possible of the liquid has been distilled over (1½–2 hours). What gases are given off? Why was mercuric sulphate (or oxide) used? Remove the substance from the neck of the retort and add it together with the mixture in the receiver to a porcelain dish containing 300 grams of cracked ice with stirring. Filter off the anhydride on a Buchner funnel, wash it with ice water until free from sulphuric acid and dry in the air on drying paper. The solid is then resublimed as follows: It is placed in a watch glass which rests on the edge of a circular opening (1 in. diam.) in an asbestos board which in turn is placed over a piece of wire gauze. A filter paper, punctured with small holes with the small blade of a pen-knife is placed over the watch glass and fitted tightly around the edge. A beaker is inverted over the watch

¹ Exercise great care in working with hot conc. sulphuric acid.



glass. The watch glass is then heated *very gently*, using a small flame. Needles form above the filter paper. Should these begin to melt decrease the heat. Save a specimen of the sublimed material. Determine its melting point and solubility. How could you test for phthalic anhydride? (See Fluorescein.)

Dissolve about a gram of the anhydride by boiling it with a small amount of water in a 250 cc. Erlenmeyer flask, using an ebulator tube and filter the solution if necessary. What is present in this solution? Let stand over night. If no crystals appear, concentrate the solution. Filter off the crystals and determine the melting point, crystal form, color, taste and solubility. Is the substance an acid? What does phthalic anhydride give when heated with alcohol? Save a specimen of phthalic acid.

EXPERIMENT 67

SALICYLIC ACID

Boil 10 cc. of oil of wintergreen with 100 cc. of a 20% solution of sodium hydroxide in a round bottom flask connected with a reflux condenser until it has all disappeared. What is formed? When cool, acidify with hydrochloric acid. Filter off the precipitated substance, recrystallize it from hot water and determine its melting point, color, crystal form, solubility and taste. What change takes place when some of the substance is carefully heated in a dry test tube? What are the products? Dissolve some of the acid in water, and add a few drops of a solution of ferric chloride. What takes place? Add a few drops of bromine water to an aqueous solution of salicylic acid and note what takes place. Explain. Save a specimen of the acid.

For what purposes is salicylic acid used?



EXPERIMENT 68

ACETYL SALICYLIC ACID

(Aspirin)

Heat 5 grams of salicylic acid with 8 grams of acetic anhydride and 1 cc. of concentrated sulphuric acid in a small flask in a water bath raising the temperature gradually to 90° or until all the salicylic acid goes into solution. Pour the solution while hot into 100 cc. of cold water containing 100 grams of cracked ice. What is the precipitate? Filter off the precipitate on a Buchner funnel, wash with ice water and dry in the air on drying paper. Recrystallize from benzene and determine its melting point, solubility, color, crystal form and taste. Treat 0.1 gram of the substance with 5 cc. of alcohol and dilute with 20 cc. of water. Add to the mixture a drop of ferric chloride solution. Is there any color formed? Explain. (See Salicylic acid.) What does it give when boiled for some time with water? Test the boiled solution with a drop of ferric chloride solution. Is aspirin an acid? Shake some of the aspirin with water and a little calcium carbonate. Filter and test the filtrate for calcium with an ammonium oxalate solution. Explain. Save a specimen of the crystallized aspirin. For what purpose is it used?



EXPERIMENT 69

SALICYLIC AND PARAHYDROXY BENZOIC ALDEHYDES

Dissolve 160 grams of sodium hydroxide by heating with 160 cc. of water in a liter round bottom flask and add 50 grams of phenol. Cool the contents of the flask to 60° – 65° by immersing in cold water and connect the flask with a reflux condenser and a thermometer, the bulb of which dips below the surface of the liquid. Add 40 grams of chloroform *gradually* (5 cc. at a time) through the inner tube of the condenser and shake the flask gently. The liquid becomes red and the temperature rises. When it reaches 70° , cool the flask in water till the thermometer indicates 65° . During the entire reaction the temperature should be kept between 65° – 70° . After waiting 10 to 15 minutes add 40 grams more of chloroform in the same manner as described above. Finally after about half an hour add 40 grams more of chloroform, taking care to keep the temperature between 65° – 70° by heating in a water bath. Frequent shaking of the mixture is essential for the success of the experiment. When the reaction is complete (about 2 hours) distil off the unused chloroform with steam. The red alkaline fluid in the flask is then allowed to cool and acidified carefully with dilute sulphuric acid when it becomes nearly colorless. Then distil with steam until oily drops no longer distil with the water. Save the contents of the flask from which the oil was distilled. Extract the aqueous distillate with ether, separate it from the water and distil off the ether, *observing the usual precautions*. The oil which remains is a mixture of unchanged phenol and salicylic aldehyde. The salicylic aldehyde is separated from the phenol by treating the mixture with twice its volume of a concentrated solution

of sodium bisulphite (made by dissolving 56 grams of powdered sodium acid sulphite in 100 cc. of water at room temperature). On stirring with a glass rod the sodium bisulphite compound of the salicylic aldehyde crystallizes out. After standing for some time the crystals are filtered off on a Buchner funnel and washed several times with alcohol and then with ether to remove the phenol. The crystals are then decomposed by warming on the water bath with dilute sulphuric acid. When cold, extract the salicylic aldehyde with ether, separate the ether extract from the dilute sulphuric acid, dehydrate it with anhydrous sodium sulphate and distil off the ether with the usual precautions. The aldehyde is then distilled, noting the boiling point. Determine odor, color, specific gravity and solubility of the substance and save specimens of it and its bisulphite compound.

Filter the contents of the flask from which the oil was distilled (see above) through a wet filter and saturate the clear filtrate with salt. Filter off the *p*-hydroxy benzoic aldehyde and extract the filtrate with ether. Evaporate the ether and crystallize the combined quantity of the aldehyde from water after adding sulphur dioxide. Determine the melting point, color, crystal form and solubility of the *p*-hydroxy benzaldehyde and save a specimen of the substance. Does its aqueous solution give any color with ferric chloride solution? Does the aqueous solution of salicylic aldehyde give any color with this reagent?

EXPERIMENT 70

PARAROSANILINE

Heat 1 gram of a mixture of freshly distilled aniline and paratoluidine (2 molecules of aniline and 1 of paratoluidine) in a small flask with 3 grams of powdered mercuric chloride and 2 grams of freshly distilled aniline in a bath of Crisco or conc. sulphuric acid (hood) to 180° – 200° for $1\frac{1}{2}$ to 2 hours. Take the temperature by means of a thermometer dipping into the fluid in the flask and use the thermometer to stir the mixture. What is formed? Extract the mixture in the flask several times with alcohol, filter and evaporate the filtrate to dryness on a water bath. Does an aqueous solution of the substance dye wool, silk or cotton? Save a specimen of the colored aqueous solution and specimens of the dyed cloth.

EXPERIMENT 71

FLUORESCEIN

Grind together in a mortar 15 grams of phthalic anhydride and 22 grams of resorcinol and heat the mixture in a nickel crucible in a Crisco bath to 180° . Then add 7 grams of powdered fused zinc chloride *slowly* and stir the mixture with a glass rod. Increase the temperature to 210° and continue the heating at this temperature until the fused mass solidifies.

Cool the crucible, remove the fused mass by mechanical means, dissolve it in dilute caustic soda solution, filter and precipitate the fluorescein from the boiling solution with conc. hydrochloric acid. Filter off the precipitate on a Buchner funnel and dry at 80° . Does the alkaline solution fluoresce? Dilute and note the dilution at which the solution becomes colorless. Heat 2 grams of the fluorescein with acetic anhydride until it all goes into solution. Cool and pour into water. Filter off the diacetate after it solidifies and recrystallize it from alcohol. Determine its melting point. Note that while fluorescein is colored the diacetate is colorless. Explain. Save a specimen of the fluorescein and of the diacetate. Use the rest of the fluorescein in Experiment 72.

EXPERIMENT 72

EOSIN AND SOLUBLE EOSIN

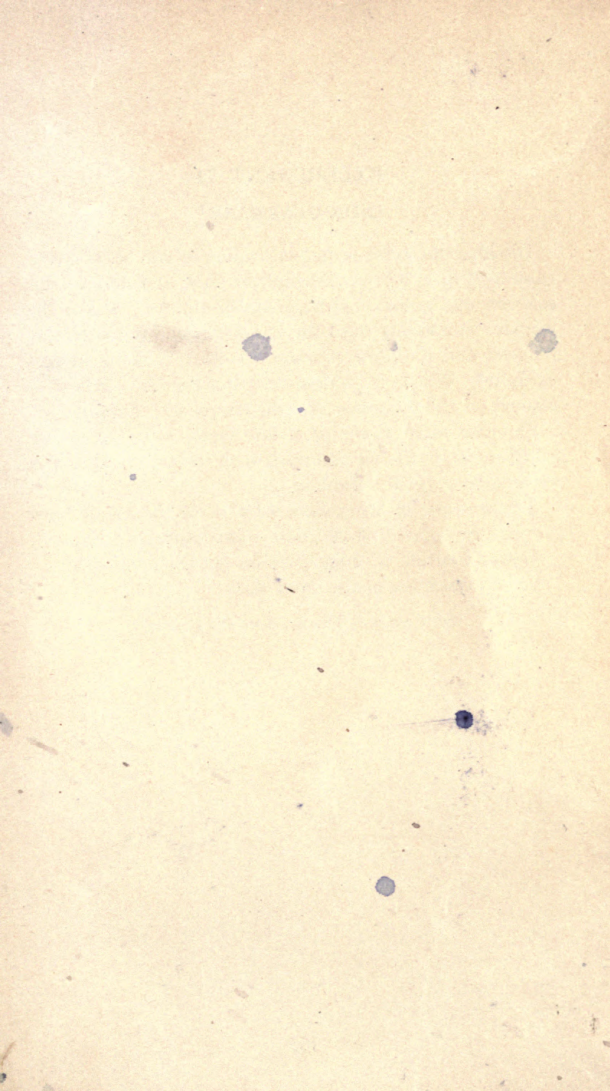
Put 15 grams of fluorescein and 60 grams of alcohol into a 250 cc. Erlenmeyer flask. Drop in *slowly*, from a small separatory funnel, 33 grams (11 cc.) of bromine, shaking the mixture in the flask. When about half the bromine has been added a clear, dark-red solution results. What is present in this solution? On further addition of bromine brick-red leaflets separate. What is this product? After standing for 2 hours the crystals are filtered off, washed with alcohol and dried in the air on drying paper. Heat a small portion of the crystallized eosin in a porcelain dish to 110° in an air bath and note any change of color. Save a specimen of the crystallized eosin and convert the rest into the sodium salt (soluble eosin). For this purpose grind 6 grams of eosin with 1 gram of anhydrous sodium carbonate in a mortar. Place the ground mixture in a 200 cc. beaker and moisten it with a little alcohol. Add 5 cc. of water and heat on the water bath until the evolution of carbon dioxide ceases. Then add 20 grams of alcohol, heat to boiling and filter the hot solution. On standing the soluble sodium salt crystallizes. Save a specimen of the soluble eosin.



EXPERIMENT 73

CRYSTAL VIOLET

Mix 5 grams of dimethylaniline, 2 grams of Michler's Ketone (tetramethyldiamino benzophenone) and 2 grams of phosphorus oxychloride in a 1 liter R. B. flask. Heat the flask (Hood) for 5 hours in an actively boiling water bath. Then add 300 cc. of water and a solution of caustic soda until the mixture is distinctly alkaline and subject it to steam distillation to remove any unchanged dimethylaniline (test some of the last aqueous distillate with bromine water and some of the first aqueous distillate with the same reagent). Cool and filter off the color base (carbinol) on a Buchner funnel, wash it with water, put it in a 500 cc. flask and then boil it with 200 cc. portions of a mixture of 1 liter of water and 5 grams of conc. hydrochloric acid. Filter the hot solutions from the undissolved color base and continue the extraction until almost all of the substance has been dissolved. Cool the combined filtrates and add pulverized salt as long as it dissolves freely, stirring the solution constantly during the addition. Is the dye precipitated? What is this process called? Filter off the dye on a Buchner funnel and recrystallize it from a small amount of hot water. Is the dye soluble in water? Does the aqueous solution give a precipitate with a solution of caustic soda? Is the *color base* of crystal violet *colored*? What takes place when this color base dissolves in dilute hydrochloric acid? Does crystal violet dye wool, silk or cotton? Save specimens of crystal violet and of the dyed cloth.



EXPERIMENT 74

INDIGOCARMINE¹

Dissolve one gram of indigocarmine in 250 cc. of water contained in a 500 cc. Erlenmeyer flask and add to this solution one gram of sodium hydrosulphite. Shake the mixture thoroughly until the indigocarmine is completely reduced and a yellow solution results. What is indigocarmine? What is sodium hydrosulphite? What is formed on the reduction of indigocarmine? Explain.

Saturate some pieces of cheese cloth with the yellow solution, dry in the air and wash with water. Is the cloth permanently dyed? Explain.

Expose some of the yellow solution to the air or blow air through some of it and note what happens. Explain.

Does a solution of indigocarmine dye wool and silk?

Save a specimen of the dyed cloth.

¹See Cain and Thorpe, *Synthetic Dyestuffs*.

EXPERIMENT 75

BENZIDINE FROM NITROBENZENE

Eight grams of sodium hydroxide are dissolved by heating with 5 to 10 cc. of water in a 250 cc. Erlenmeyer flask and 50 cc. of alcohol are added. Add 4 cc. of nitrobenzene, *warm gently* on an asbestos board with a circular opening $\frac{1}{2}$ inch in diameter placed over a piece of wire gauze and add *slowly* 10 grams of zinc dust in small portions, waiting for any action to cease before a new portion is added. Note the color change. When all the zinc dust has been added, connect the flask with a cork and reflux condenser and boil the contents until no red oil is formed when a little of the solution is poured into 10 cc. of dilute sulphuric acid contained in a test tube. The reaction is then complete. The solution is poured into an excess of dilute sulphuric acid and heated to boiling. What is the precipitate formed? Cool and filter off the precipitate on a Buchner funnel, wash with water and recrystallize some of the product from boiling water. Is it very soluble in water?

Boil the rest of the salt with an excess of a solution of caustic soda, filter the solution while hot and let stand till cold. What is the product which crystallizes out? Filter, wash with water and recrystallize the product from boiling water. Filter off the recrystallized product, wash with water and dry in the air on drying paper. Determine its melting point and solubility. Dissolve a small amount of the benzidine in boiling water in a test tube and add a solution of potassium bichromate. Note what takes place. Is this reaction characteristic of benzidine? Save specimens of the crystallized sulphate and of the crystallized benzidine. How is benzidine converted into diphenyl? For what purpose is benzidine used commercially?

EXPERIMENT 76

ORANGE II

Dissolve 5 grams of crystallized sulphanilic acid in dilute caustic soda solution, adding the caustic soda solution carefully and taking care not to have an excess present. The volume of the liquid should be about 200 cc. Ice is added and the mixture is stirred until the temperature is about 5°. Add 10 cc. of conc. hydrochloric acid and then slowly through a separatory funnel a solution of 2.5 grams of sodium nitrite in 25 cc. of water, testing from time to time a drop of the solution with starch-iodide paper to see when an excess of nitrous acid is present and keeping the temperature about 5° by stirring. What compound crystallizes out?

Dissolve 3 grams of β -naphthol in a solution of 1 gram of caustic soda dissolved in 10 cc. of water, dilute with 50 cc. of water and cool to 15°. Add the suspension of the diazonium salt gradually, stirring the solution and keeping the temperature at about 15°. When all the diazonium salt has been added the mixture should have a slight alkaline reaction¹ and should be allowed to stand for an hour. Add some saturated salt solution to precipitate the rest of the dye, filter off the precipitate on a Buchner funnel, and dry at 80°. Is the dye soluble in water? Does its solution give a colored precipitate with hydrochloric acid? Explain. Does it dye wool and silk from an acid bath? Save specimens of the dye and of the dyed cloth.

¹Test with brilliant yellow paper. If it is not alkaline, make it alkaline.

EXPERIMENT 77

ANTHRAQUINONE

(Hood)

Cover 5 grams of anthracene with six to eight times its weight of alcohol (so that on boiling the alcohol only part of the anthracene dissolves), then pass a strong current of chlorine¹ into the *boiling* liquid. After some time a solution is obtained, which on further addition of chlorine gives a precipitate (?). After cooling, filter, wash the precipitate with cold alcohol, then with dilute caustic soda solution, and finally with water, dry, and sublime.

Determine color, crystal form, melting point and solubility of the substance. Warm one part of the substance with zinc dust (2 parts) and caustic soda solution (30 parts of 50% solution). What takes place? Explain. Save a specimen of the anthraquinone. How is anthraquinone made technically?

¹ Use a wide delivery tube. Wear goggles.



EXPERIMENT 78

ALIZARIN

(Hood)

Heat 20 grams of anthraquinone in a $\frac{1}{2}$ liter long neck flask with 25 grams of fuming sulphuric acid (45 to 50% SO_3) gradually in a Crisco bath to 160° for one hour. What is formed? Pour the mixture cautiously into 2 liters of hot water contained in a porcelain dish, stirring the water vigorously. Boil for a few minutes and filter the solution to remove any unchanged anthraquinone.¹ Warm the filtrate and add solid sodium carbonate *gradually* with stirring until the solution has a neutral reaction. If on cooling the sodium salt does not crystallize out, concentrate the solution. Filter off the sodium salt. Save a specimen of the crystallized "silver salt" and convert the rest into alizarin. For this purpose dissolve one part of the "silver salt" in as small a quantity of hot water as possible in an autoclave, add 5 parts of solid caustic soda and 0.2 parts of potassium chlorate. Close the autoclave and heat the mixture for 20 hours at 170° . Cool and remove the melted mass by boiling with water and by mechanical means. Saturate the boiling solution in a porcelain dish with concentrated hydrochloric acid, boil for fifteen minutes, filter off the precipitate on a Buchner funnel while hot and wash it with hot water until the hydrochloric acid is removed. Dry and sublime. What is this substance? Determine its color, melting point, crystal form and solubility. Does it dissolve with color in alkalis? Explain. Does it dye cotton? What colors does it give with the different mordants? What is formed by heating some with ten times its weight of zinc dust in a test tube? Save a specimen of the alizarin.

¹The anthraquinone recovered should be washed with water till free from acid, dried in the air on drying paper and put in the bottle labeled "Recovered Anthraquinone."



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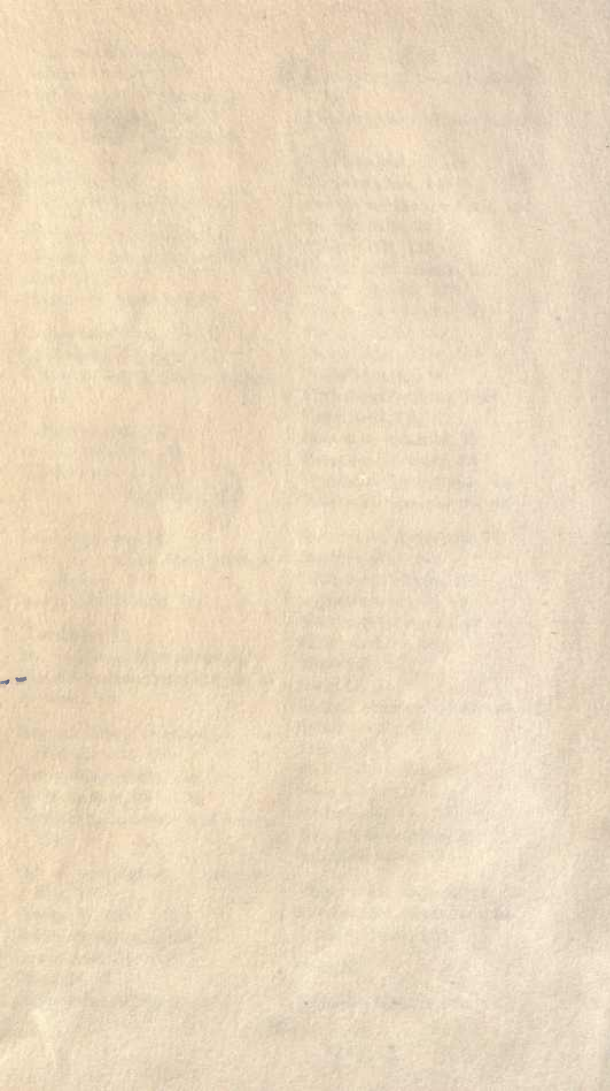
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